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# RUBBER CHEMISTRY AND TECHNOLOGY

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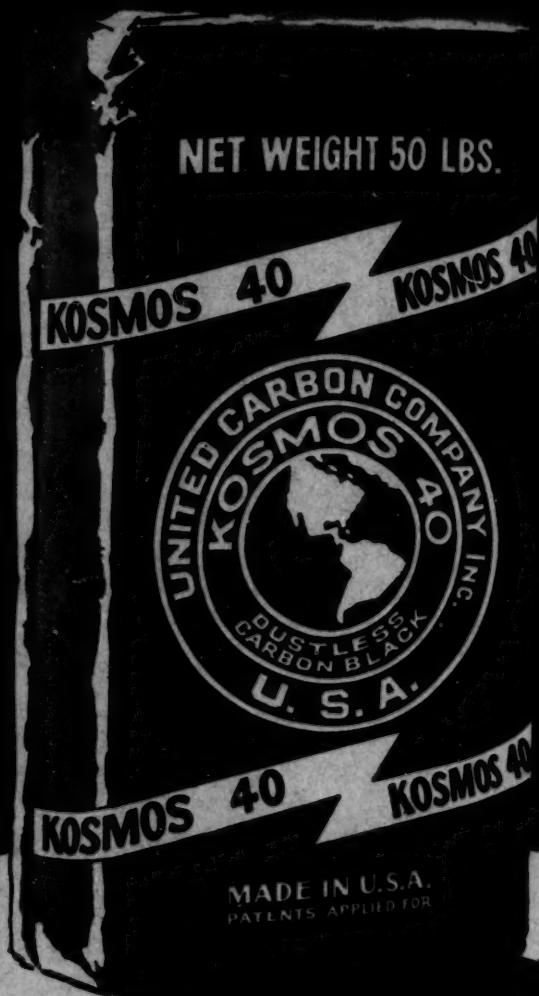


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# RUBBER CHEMISTRY AND TECHNOLOGY

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## RUBBER CHEMISTRY AND TECHNOLOGY

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## SODIUM-CATALYZED COPOLYMERIZATION OF 1,3-BUTADIENE AND STYRENE \*

C. S. MARVEL, W. J. BAILEY, AND G. E. INSKEEP

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### INTRODUCTION

The use of sodium as a catalyst for the polymerization of butadiene in the liquid phase has been known for many years<sup>1</sup>. Its use as a catalyst for the copolymerization of butadiene and styrene by the procedure used to make Buna-85 has been suggested in a patent<sup>2</sup>, but no record of the actual achievement of this copolymerization is available. In fact, recent discussions with research chemists of I. G. Farbenindustrie have indicated that no such copolymerization has been carried out there. The polybutadiene made by sodium polymerization is known to have properties that are different from those of emulsion polybutadiene. We undertook the study of the copolymerization of butadiene and styrene in the hope of obtaining a polymer with properties different from those of GR-S.

The present paper reports the successful use of sodium as a catalyst for the copolymerization of butadiene (75 parts) and styrene (25 parts). The purity of the monomers used is critical, and it appears to be the improvement in this respect which has led to our success. The properties which will be described later indicate that a true copolymer and not a mixture of polymers was obtained in our experiments. We describe in this paper some of the variables which affect the rate of polymerization and the character of the copolymer. In a subsequent manuscript the industrial evaluation of this copolymer will be presented.

### GENERAL PROCEDURE

The polymerizations were carried out in screw-cap bottles, into which were introduced the catalyst, styrene, and butadiene, successively; the butadiene was allowed to boil for a short time to flush out the air, and the bottles were capped tightly with tops fitted with tinfoil-lined rubber gaskets. The bottles were rotated end-over-end in a water bath maintained at constant temperature until solidification of the contents indicated that the polymerization was complete. The polymeric product was swollen with benzene containing antioxidant, and then the sodium was destroyed with alcohol. More benzene was added to the mixture to dissolve the polymer, and methanol was added until the product had been precipitated. The moist polymer was mixed with additional antioxidant and dried for six to eight hours at 70–80° C.

### EXPERIMENTAL

*Catalyst preparation.*—A clean piece of sodium weighing about 200 mg. was placed in a weighing bottle filled halfway with dry toluene; the bottle was then

\* Reprinted from the *Journal of Polymer Science*, Vol. 1, No. 4, pages 275–288, August 1946. The investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government synthetic rubber program.

weighed to the nearest milligram. The surfaces of the lump of sodium were cut off to form a shiny lump weighing about 100 mg. The exact weight of this freshly cut piece of sodium was determined by weighing the bottle after the next transfer. A 10-inch length of 8 mm. glass tubing was sealed at one end and thoroughly dried. It was filled to a depth of 3 inches with dry toluene, the sides of the tube were dried, and the tube was flushed out with nitrogen. The weighed sodium was then introduced; the tube was again flushed out, capped, cooled in dry ice, and sealed. It was allowed to stand to make sure that any oxygen or water present had reacted with the sodium, so that the sand would be formed in an inert environment. The tube was immersed in an oil bath at about 140° C, then removed, shaken very vigorously by hand to disperse the sodium, and tilted back and forth gently while the mixture cooled and the sodium solidified. This process was repeated, if necessary, until a suitable dispersion was obtained.

*Monomers.*—Butadiene (except where noted) was the Research Grade or Special Purity Grade supplied by Phillips Petroleum Company, with a minimum purity of 99.7 per cent. It was passed through a tower containing sodium hydroxide pellets and condensed in a dry-ice trap immediately before use.

Styrene was the commercial grade supplied by Dow Chemical Company and designated as N-100. It was washed with 10 per cent sodium hydroxide to remove the inhibitor, then with an equal volume of Nessler's reagent to extract any phenylacetylene. The styrene was filtered through a cotton plug, dried over anhydrous magnesium sulfate, and distilled through a 12-inch Vigreux column without reflux at a rate of approximately one drop per second. The first 10 per cent of distillate was added to the next batch, with any water still present; the last 5-10 per cent of the charge remained as residue.

It has recently been established that preliminary washing is unnecessary, but all styrene has been subjected to that treatment.

*Polymerization with sodium sand.*—The tube containing the sodium sand was broken open and the contents were poured into a clean, dry, butadiene-flushed, 4-oz. screw-cap bottle, whose lip had been inspected for freedom from irregularities. The tube was rinsed with an additional 2-8 cc. of dry toluene, depending on the amount of catalyst used. The 4-10 cc. of toluene used in the preparation and transfer of the catalyst was always present during the polymerization. As indicated in later experiments, using larger amounts of toluene and no toluene at all, the effect of toluene on the polymerization seems to be very slight. The usual catalyst concentration was 0.35 part per 100 parts of monomer. An amount of monomer previously calculated from the weight of catalyst was weighed into the bottle with a precision of approximately 0.1 gram. A small excess of butadiene was added, and was then allowed to boil off to remove air before the cap was put on. The cap was gasketed with a rubber disk (1.5-2.0 mm. thick) covered with a heavy tinfoil disk.

Polymerization was carried out in a bath with temperature regulation accurate to  $\pm 0.5^\circ$  C. The bottles were rotated end-over-end 27 times per minute (50 times per minute in the case of polymerizations at 50° C) until the reaction seemed to be complete, as indicated by solidification of the contents.

*Separation of the polymer.*—Benzene containing 10% absolute alcohol and a trace of phenyl- $\beta$ -naphthylamine as antioxidant was added to the product in the bottle. The mixture was removed and added to a large excess of benzene to give a homogeneous dispersion. The polymer was precipitated with methanol and pressed free of liquid, then mixed with more antioxidant. Drying was accomplished in 6-8 hours in a circulating-air oven at 70-80° C.

*Characterization of the polymer.*—The solubility of the material was usually determined by allowing a 0.4-gram sample, which had been cut into small pieces, to stand for 48 hours in 100 cc. of dry benzene in a closed bottle at room temperature. The liquid was decanted and filtered through 80-mesh screen to remove gel; a 10-cc. aliquot was pipetted into a tared aluminum pan. When the solvent had evaporated, the pan was dried for two hours in a circulating-air oven at 70–80° C and weighed. The solubility in benzene as determined by this method gives the amount of the polymer that is not gel.

The gel-free solution was diluted with 10 parts of dry benzene and its flow time was measured in an Ostwald viscometer at 25° C. From this value and the flow time for dry benzene the intrinsic viscosity,  $[\eta]$ , was computed by the following formula:

$$[\eta] = (\ln t - \ln t_0)/c$$

where  $t$  and  $t_0$  are the flow times of the solution and solvent and  $c$  is the concentration of polymer in grams per 100 cc. of solution.

The solutions of a few samples were prepared by the less accurate method of tumbling the bottles containing the polymer and benzene for 12 hours in an air oven at 38° C. Loose gel is often colloiddally dispersed by this procedure.

#### GENERAL DISCUSSION

There are two distinct phases of polymerization. During the induction period no increase in viscosity of the monomer is observed; this period varies in length, but is ordinarily longer than the one which follows. The period of actual polymerization first makes itself known by cohesion between the catalyst particles. The particles become surrounded by a clear, solid gel, so that the mass bears a strong resemblance to frog eggs. Meanwhile the liquid phase becomes more viscous and when reaction is complete the contents are entirely converted to a transparent solid. These two periods for butadiene alone at 30° C are in the neighborhood of ten and four hours, and those for a 75:25 mixture of butadiene and styrene at the same temperature, are roughly six and four hours, respectively. Since the conversion is quantitative, it is evident that the rate even at this low temperature is extremely rapid.

This high rate causes considerable generation of heat in a short time and, if this is not dissipated, it may be detrimental to the polymer and may also produce uncontrollable pressures. Thus, any substance which would further catalyze the reaction is undesirable. Two serious explosions which occurred in our earlier experiments may have been the results of such catalysis. As far as could be determined, these runs were normal in every respect except for prolonged heating of the sodium during the catalyst preparation and the appearance of a pinkish color in the toluene near the catalyst surface, although the sand was clean and bright; at the end of three hours at 30° C these butadiene polymerizations exploded violently. In a companion run the pressure was released through a broken gasket, and it was possible to determine that the conversion was well above 50 per cent in six hours. Although this product was benzene-soluble, polybutadienes prepared without agitation or in large batches (150 grams in 500-cc. bottles), so that heat transfer was reduced, were found to be partially insoluble; moreover, the product from the large-scale preparation could be separated into a highly insoluble, darkened core and a partially soluble, outer shell (Table I). Normal runs are included in the table for comparison.



TABLE I  
RESULTS OF POOR HEAT EXCHANGE IN BUTADIENE POLYMERIZATION

Run No.	Cause of overheating	Bath temperature (° C)	Solubility in benzene (%)	[ $\eta$ ]
255	None	30	95	5.46
13	None	10	95*	5.17
66	Not agitated	20	74	8.32
67	Not agitated	10	83	7.33
62 (core)	Large run	30	19	1.26
62 (shell)	Large run	30	59	2.40
64 (core)	Large run	20	26	1.16
64 (shell)	Large run	20	55	4.83

\* This solubility was measured by the tumbling method.

The purity of the butadiene appears to be highly important. Two runs in which Shell Oil Company butadiene with a minimum purity of 98 per cent was used did not show any sign of polymerization after three weeks at 30° C. The effect of individual known impurities will be discussed later.

*Standard 30° polymerization.*—Representative polymerization of butadiene and butadiene-styrene (75:25) mixtures at 30° are listed in Table II. This was the temperature most frequently used because it gave a reasonable conversion rate without unduly high pressures. The abbreviations S-B and S-BS have been coined for the polymer and copolymer, respectively.

TABLE II  
TYPICAL S-B AND S-BS POLYMERIZATIONS AT 30° C

Run No.	Polymer	Polymerization time (hrs.)	Conversion (%)	Solubility in benzene (%)	[ $\eta$ ]
9	S-B	21	95	93*	6.36
11	S-B	12.5	81	96*	6.74
12	S-B	15	91	97*	6.43
26	S-B	10	100	89*	6.88
38	S-B	17	100	93	6.16
255	S-B	14	100	95	5.46
256	S-B	13	100	96	5.07
295	S-B	10.5	100	100	5.09
22	S-BS	10	100	100*	7.01
23	S-BS	15	100	91*	7.51
41	S-BS	< 8	100	90	5.07
44	S-BS	< 8	100	95	5.79
283	S-BS	9.5	100	92	4.45
340	S-BS	8	100	87	3.38

\* Solubilities measured by the tumbling procedure.

The variability in rate and product is not surprising in view of the sensitivity to impurities which has been observed. The importance of eliminating foreign substances to obtain a uniform polymer cannot be overemphasized.

*Interrupted 30° polymerization.*—When it became desirable to prepare the polymer in batches larger than 40 grams, two procedures were devised which were successful in providing good heat removal and thus in producing soluble rubbers. In the first, a charge of roughly 125 grams of monomers in an 8-oz. bottle was rotated at 30° until polymerization was well under way and the mass had become quite viscous. The bottle was then immersed in ice water until chilled and left in water at room temperature without further stirring until solidification showed that the conversion was complete. The chilling prevented



overheating when heat transfer had become slow, yet the polymerization was far enough advanced to continue without an appreciable change in the total time. With few exceptions, the products were soluble and of nearly normal viscosity (Table III), although the viscosities showed considerable variation.

TABLE III

S-B AND S-BS POLYMERIZATIONS AT 30° C AND INTERRUPTED BY CHILLING IN ICE

Run No.	Polymer	Polymerization time (hrs.)	Conversion (%)	Solubility in benzene (%)	$[\eta]$
217	S-B	14	100	100	3.44
219	S-B	13	100	96	4.78
222	S-B	13	100	98	5.58
224	S-B	13	100	99	3.30
226	S-B	15	100	99	2.26
229	S-B	11	100	96	6.50
63	S-BS	15	100	96	4.78
161	S-BS	9	100	98	4.65
165	S-BS	9	100	98	3.62
169	S-BS	11	100	100	3.43
181	S-BS	12	100	99	3.76
184	S-BS	10	100	99	5.34
185	S-BS	12	100	94	2.78
194	S-BS	12	96	97	5.12
207	S-BS	13	100	85	3.10
211	S-BS	12	100	98	4.18

*Increment addition of monomers.*—The second procedure to avoid overheating was slower and somewhat less effective. To 350–450 mg. of sodium sand (enough for 100–130 grams of monomer) in an 8-oz. bottle was added 25 grams of monomer. This charge was rotated at 30° C until the liquid phase had disappeared; the bottle was opened, another 25 grams of monomer was added, and rotation was resumed until this liquid had disappeared. The procedure was repeated until the time for polymerization became excessively long; after the last addition, rotation was continued for 24 hours. Conversions were seldom quantitative and the products were not wholly soluble. Table IV lists the properties of products prepared by this method.

TABLE IV

S-B AND S-BS POLYMERIZED IN 25-GRAM INCREMENTS AT 30° C

Run No.	Polymer	Conversion (%)	Solubility in benzene (%)	$[\eta]$	Time for each polymerization (hrs.)
116	S-B	73	90	5.36	14, 16, 18, 18, 22
118	S-B	85	85	4.85	17, 16, 17, 18, 18, 20
136	S-BS	94	89	5.35	9, 10, 8, 9, 10
137	S-BS	82	92	5.23	9, 10, 8, 9, 10
138	S-BS	90	86	4.81	12, 10, 12, 30
139	S-BS	86	91	4.52	12, 8, 6, 8, 10, 10
140	S-BS	85	93	4.79	12, 8, 6, 8, 10, 12
141	S-BS	92	93	4.58	12, 8, 6, 8, 18
142	S-BS	82	83	4.72	8, 6, 8, 10, 8, 10
143	S-BS	93	78	5.04	12, 8, 8, 8, 10, 8
144	S-BS	86	80	4.44	12, 8, 6, 8, 10, 8
145	S-BS	88	87	4.40	12, 10, 10, 22
146	S-BS	73	93	3.50	12, 10, 12, 30
147	S-BS	95	86	4.55	12, 10, 12, 22
148	S-BS	87	96	4.32	12, 8, 10, 24
149	S-BS	90	78	4.42	12, 10, 10, 10, 24

*Addition of diluents.*—Polymerization in a diluent should be a convenient means of controlling the temperature and facilitating removal of the finished polymer. Unfortunately, it has been found that the amount of diluent necessary to give a fluid dispersion of the final product is so great that the polymerization time is multiplied several-fold and the molecular weight of the polymer is so reduced that the product is soft and tacky. Attempts to cut down the polymerization time by increasing the amount of catalyst were partially successful, but the viscosity of the rubber was still further diminished. More investigation will probably show the proper diluent and concentration to produce a good rubber at a reasonable rate. It was found that replacing toluene used in the preparation of catalyst with either *n*-hexane or methyleyclohexane did not change the rate of polymerization or the properties of the polymer. Furthermore, adding a volume of toluene equal to the volume of the monomers used (Run 89, Table V) had little effect on the polymerization rate or the quality of the polymer.

Experiments on solution polymerization are summarized in Table V. All diluents were dried over sodium before use.

TABLE V  
POLYMERIZATION IN DILUENTS AT 30° C  
(Conversion complete, products soluble)

Run No.	Polymer	Diluent	Approximate ratio diluent: monomer	Polymeriza- tion time (hrs.)	[ $\eta$ ]
295	S-B	None	...	10.5	5.09
89	S-B	Toluene	1:1	14	4.98
297	S-B	<i>n</i> -Heptane	1.5:1	16	5.05
298	S-B	<i>n</i> -Heptane	1.5:1	<30	2.13
299	S-B	<i>n</i> -Heptane	4:1	144	0.68
300	S-B	<i>n</i> -Heptane	4:1	180	0.66
283	S-BS	None	...	9.5	4.45
347*	S-BS	<i>n</i> -Heptane	2:1	34	0.73
348*	S-BS	<i>n</i> -Heptane	2:1	<40	0.64
351*	S-BS	<i>n</i> -Pentane	2:1	<40	0.27
352*	S-BS	<i>n</i> -Pentane	2:1	30	0.62
345*	S-BS	<i>n</i> -Heptane	4:1	74	0.30
346*	S-BS	<i>n</i> -Heptane	4:1	<75	0.41
349*	S-BS	<i>n</i> -Pentane	4:1	54	0.28
350*	S-BS	<i>n</i> -Pentane	4:1	59	0.23

\* Three times the normal amount of catalyst.

† Six times the normal amount of catalyst.

*Catalyst concentration and particle size.*—The effect of increased catalyst concentration on solution polymerization has already been mentioned (Table V). Many other variations in the concentration and particle size of the sodium were tested; the results are given in Table VI. The net effect of either a reduction in concentration or an increase in particle size is a reduction in the exposed surface. The use of sodium wire has in addition the effect of concentrating the catalyst in one locality, for the wire soon forms a ball which becomes the nucleus of a polymer mass. Only a large decrease in the catalyst concentration causes an appreciable drop in polymerization rate, but the reduction in exposed surface shows up readily in increased viscosity and (although not so markedly) in lower solubility in benzene, both of which are indications of increasing molecular weight. The increase in molecular weight clearly results from the formation of fewer active centers. The lack of correlation between

rate and catalyst surface is not so easily explained, but it seems to indicate that initiation is not the rate controlling step.

*Effect of temperature.*—Temperature change has an inexplicable effect on the polymerization<sup>4</sup>. At 10° C (see Table VII) the overall time was very much longer than at 30°, but the product at 10° was apparently identical with that at 30°; at 50° the total time was very little less than at 30°, but the polymer had a markedly lower viscosity. Most of the decrease in polymerization time from 30° to 50° was accounted for by a shortened induction period.

TABLE VI

EFFECT OF CHANGES IN CATALYST SURFACE ON BUTADIENE POLYMERIZATION AT 30° C  
(Conversion complete)

Run No.	Catalyst	Catalyst concentration (%)	Catalyst area	Polymerization time (hrs.)	Solubility in benzene (%)	[ $\eta$ ]
38	Normal	0.35	Normal	17	93	6.16
255	Normal	0.35	Normal	14	95	5.46
18	Normal	0.30	Normal	<12	89	7.97
19	Normal	0.30	Normal	15	91	5.35
20	Normal	0.20	Slightly low	<12	89	4.93
21	Normal	0.20	Slightly low	<12	85	7.26
105	Normal	0.04	0.1 normal	21	84	7.67
106	Normal	0.04	0.1 normal	<48	81	5.24
109	Normal	0.04	0.1 normal	28	69	6.06
110	Normal	0.04	0.1 normal	20	89	7.69
107	Normal	0.02	0.05 normal	28	77	7.20
111	Normal	0.02	0.05 normal	23	82	6.53
112	Normal	0.02	0.05 normal	<48	41	6.54
25	Fine sand	0.35	Large	12	97	4.86
78	Fine sand	0.35	Large	15	98	5.41
79	Fine sand	0.35	Large	17	96	5.67
76	Coarse sand	0.35	Small	17	97	6.37
77	Coarse sand	0.35	Small	15	92	7.39
24	Coarse sand	0.35	Small	12	80	7.54
159	4 ft. of wire*	0.15	Very small	18	63	8.40
157	1 ft. of wire*	0.04	Very small	20	56	8.30
158	1 ft. of wire*	0.04	Very small	18	63	7.65
160	1 ft. of wire*	0.04	Very small	16	73	7.64

\* Diameter, 0.25 mm.; concentration estimated.

The time of polymerization at 50° shows good reproducibility within a series run simultaneously, but is quite variable from one series to the next. The S-BS information in Table VII is a composite of runs selected from various series.

The preparation of large quantities of polymer by the method of increment addition was successful at 50°; S-BS made in this way was soluble but had low intrinsic viscosities (1.5–2.7). Fewer additions could be made than at 30° before an appreciable drop in rate occurred.

*Effect of added ingredients.*—The effect of certain individual compounds on rate and product quality has been investigated (Table VIII). Briefly, of the materials tested, only water<sup>5</sup> and sodium hydroxide at low concentrations were without appreciable effect; soap at intermediate concentrations and 1- and 2-butene at high concentrations merely lowered the polymer viscosity. Vinylacetylene and acetaldehyde at intermediate concentrations inhibited polymerization. These compounds are to be expected as possible impurities in butadiene. Anthracene is said to react with sodium alkyls, and it was therefore

TABLE VII  
 POLYMERIZATION AT VARIOUS TEMPERATURES

Run No.	Polymer	Polymeriza- tion (° C)	Polymeriza- tion time (hrs.)	Conversion (%)	Solubility in benzene (%)	[ $\eta$ ]
13	S-B	10	111	100	95	5.17
14	S-B	10	84	100	92	6.94
15	S-B	10	49	81	90	6.18
16	S-B	10	38	60	93	4.08
38	S-B	30	17	100	93	6.16
256	S-B	30	13	100	96	5.07
130	S-B	50	12	100	98	3.58
131	S-B	50	9	100	95	4.00
132	S-B	50	14	100	95	3.72
133	S-B	50	14	100	95	3.76
44	S-BS	30	<8	100	95	5.79
283	S-BS	30	9.5	100	92	4.45
173	S-BS	50	9	99	99	2.07
242	S-BS	50	<8	100	99	2.53
243	S-BS	50	6	100	99	2.29
248	S-BS	50	5	100	99	2.52
257	S-BS	50	<4	100	94	2.13
261	S-BS	50	4	100	93	3.07
264	S-BS	50	5	100	98	4.78
273	S-BS	50	6	100	98	3.05
277	S-BS	50	6.5	96	92	1.92
280	S-BS	50	6	100	100	1.97

tried as a modifier; at high concentrations it inhibited polymerization strongly, although it reduced the viscosity as predicted.

The compounds added were obtained in the purest form available; the volatile materials were distilled before use. The soap was a pure commercial product dried at 70° in an air oven.

 TABLE VIII  
 EFFECT OF VARIOUS COMPOUNDS ON BUTADIENE POLYMERIZATION AT 30° C

Run No.	Impurity	Impurity concentra- tion (%) <sup>*</sup>	Polymeriza- tion time (hrs.)	Conversion (%)	Solubility (%)	[ $\eta$ ]
255	None		13	100	96	5.07
82	1-Butene	15	17	100	100	4.03
83	1-Butene	15	18	100	100	2.98
80	2-Butene	15	13	61†	100	3.68
81	2-Butene	15	15	62†	100	2.90
85	Vinylacetylene	1	>500	Trace	..	..
86	Vinylacetylene	1	>500	Trace	..	..
87	Acetaldehyde	1	>400	6	97	5.56
88	Acetaldehyde	1	>400	12	98	2.34
95	Anthracene	20	240	108	74	0.60
70	Water	0.15	18	100	98	6.10
71	Water	0.09	18	85	98	5.27
72	Sodium hydroxide	0.23	19	87	96	4.40
73	Sodium hydroxide	0.23	20	100	91	5.77
74	Soap†	2.2	20	100	99	3.92
75	Soap†	2.3	18	100	99	2.78

\* On the basis of monomer + impurity.

† Thought to be 100%; may have been loss of low-molecular weight material during isolation.

‡ Procter and Gamble SF Flakes.

TABLE IX  
S-B POLYMERIZATION AT 30° C—TESTS ON PURIFIED BUTADIENE

Run No.	Butadiene	Induction (hrs.)	Time after induction (hrs.)	Conversion (%)	$[\eta]^*$
323	Standard	10	..	1	0.53
324	Standard	11	..	1	0.38
325	Distilled from polymerization	3.75	10	100	2.72
326	Distilled from polymerization	3.75	11	100	4.07
327	Distilled from polymerization	2	7.5	100	2.78
328	Distilled from polymerization	4	10	100	2.22

\* Products soluble in benzene.

An attempt was made to remove inhibitors responsible for the induction period by distilling butadiene from a partially polymerized mass. Although the induction period for the purified monomer (Table IX) had been reduced to about one-third the normal time, the total length of polymerization was practically unchanged because the rate after induction was apparently much slower. This effect was observed repeatedly. The remaining induction period may arise from traces of impurity introduced in the toluene with the catalyst, but the slower polymerization has not been explained, nor has the low viscosity of the product.

The butadiene, purified by polymerization, was distilled from the bottle in which the induction period had just ended, into a bottle previously heated and flushed with nitrogen. The sodium sand was added and the bottle was rotated at 30°.

*Effect of other metals.*—A limited study has also been made of the effect of metals which might be used in the construction of apparatus for carrying out these polymerizations on a larger scale (Table X). Some confusion was intro-

TABLE X  
EFFECT OF METALS ON BUTADIENE POLYMERIZATION AT 30° C  
(Conversion complete)

Run No.	Metal	Polymerization time (hrs.)	$[\eta]^*$
255	None	14	5.46
256	None	13	5.07
249	6 2-in. steel nails†	13	3.05
250	6 2-in. steel nails†	14	1.95
251	6 sq. in. of stainless steel screen†	12	3.48
252	6 sq. in. of stainless steel screen†	13	4.68
253	3 ft. of copper wire†	<30	3.20
254	3 ft. of copper wire†	<30	1.50
295	None	10.5	5.09
287	3 ft. of steel wire, polished (fixed in neck of bottle)	13	4.29
288	3 ft. of steel wire polished	10	2.84
289	3 ft. of steel wire polished†	10	3.41
290	3 ft. of steel wire polished†	10	2.28
291	Stainless steel screen†	11	4.55
292	Stainless steel screen†	11	4.45
293	3 ft. of copper wire†	10	1.66
294	3 ft. of copper wire†	13	1.72

\* Products soluble in benzene.

† Washed with dry benzene.

‡ Washed with hydrochloric acid and dry benzene.

duced by the agitation caused by loose pieces of metal, since this may have been responsible for the low viscosities of the products; aside from this effect, the only metal which was markedly harmful was copper wire that had not been cleaned by washing with hydrochloric acid.

All metals were washed with dry benzene before they were placed in the polymerization bottles. Some were also given a preliminary immersion in dilute hydrochloric acid for several minutes and were rinsed with water. All except the samples of screen and one piece of steel wire were free to move in the bottle, and thus to agitate the polymerizing mass.

#### AGING OF THE COPOLYMER

The behavior of the styrene-butadiene copolymer on aging is markedly different from that of GR-S; however, a sample of S-BS into which additional antioxidant had been milled was superior to GR-S on aging, and it was concluded that the dispersion of the original antioxidant was incomplete. It also seemed possible that the fat acid retained by GR-S from the emulsifying soap might be partly responsible for its good age-resistance. The sample of S-BS was accordingly milled with five per cent of the fat acid from Procter and Gamble SF Flakes and tested again. The results were somewhat surprising. Although the rubber immediately after milling was comparable with the milled sample containing no fat acid, it dropped rapidly in viscosity during the test and at the end of three weeks, when insolubilization began in both samples, it had become a soft, tacky mass with approximately half its original viscosity. This effect is entirely different from the decrease in viscosity of the sol portion of a polymer which accompanies insolubilization, and which is usually attributed to the removal of the larger molecules as part of the gel. Aging behavior is tabulated in Table XI<sup>6</sup>.

TABLE XI  
EFFECT OF AGING AT 70° C IN AN AIR OVEN ON 30° S-BS

Aging, weeks	GR-S		S-BS (unmilled)		S-BS (cold-milled)		S-BS (cold-milled) + fat acid	
	Soly. (%)	$[\eta]$	Soly. (%)	$[\eta]$	Soly. (%)	$[\eta]$	Soly. (%)	$[\eta]$
0	100	2.00	88	4.57	96	2.34	96	2.40
$\frac{1}{2}$	..	..	..	..	97	2.38	100	1.61
1	..	..	66	2.92	93	2.41	98	1.40
2	..	..	48	1.89	95	2.33	100	1.29
3	..	..	38	1.41	90	2.24	83	1.25
4	59	0.82	..	..	..	..	..	..
5	..	..	37	1.37	..	..	..	..
6	..	..	37	1.40	..	..	..	..

#### MOLECULAR WEIGHTS AND HOMOGENEITY

The high intrinsic viscosities of S-BS rubbers point to a relatively large molecular weight. This was verified by the determination of number-average molecular weights by extrapolation of osmotic pressures to infinite dilution: for 30° S-BS ( $[\eta]$  6.34), 76,900; for GR-S ( $[\eta]$  2.44), 42,200; and for the soluble 39.5 per cent of natural smoked sheet ( $[\eta]$  6.18), 60,860. A 50° S-BS ( $[\eta]$  2.07) had a molecular weight of 48,500. More significant, perhaps, in the estimation of the quality of an elastomer is its homogeneity with respect to molecular size. This is a controversial matter on which the present findings may help to shed light. It is believed by some investigators that the homogeneity of molecular



TABLE XII  
 HETEROGENEITY INDICES FOR S-B AND S-BS

Run No.	Description of polymer	Polymerization temperature (°C)	Heterogeneity index
12	S-B	30	2.61
18	S-B	30	2.45
22	S-BS	30	1.98
23	S-BS	30	1.05
308	S-BS (increment addition)	30	1.53
248	S-BS	50	4.35

weight of the soluble portion of natural rubber is in part responsible for its desirable properties; the weights of individual molecules in GR-S are more scattered. It has been shown that the molecular-weight distribution of 30° S-BS is very similar to that of natural rubber; the distribution of 50° S-BS is much the same as that of GR-S; and the homogeneity of 30° S-B is intermediate<sup>7</sup>.

On this same basis natural rubber has heterogeneity indices from 1.5 to 1.9 and GR-S from 4.4 to 12.4.

In determining the precipitation curve of a soluble polymer, the volume fraction of the precipitant,  $\phi$ , is plotted against the weight fraction of polymer remaining in solution. The heterogeneity index is defined as the difference of the average square of the volume fraction of the precipitant,  $\bar{\phi}^2$ , and the square of the average volume fraction of the precipitant,  $\bar{\phi}^2$ , where the averages are calculated by using the amount of polymer remaining in solution as the weighting factor.

#### QUANTITY OF 1,2 ADDITION

Since Ziegler, Grimm and Willer<sup>8</sup> indicated that polybutadiene prepared at 30° C with sodium had a high vinyl side-chain content, and that an increase in temperature of polymerization causes a decrease in the vinyl side-chain content, several samples of S-BS and S-B were ozonized. The formaldehyde, obtained on hydrolysis of the ozonide, was oxidized to carbon dioxide and an indication of the amount of vinyl side-chain content was calculated from the weight of carbon dioxide obtained. The results are given in Table XIII<sup>9</sup>.

 TABLE XIII  
 OZONIZATION NUMBERS OF SODIUM-POLYMERIZED POLYMERS

Sample	Description		Diene (%)	Ozonization No.†
	Temp. (°C)	Type		
22	30	S-BS	75	29.2
177	50	S-BS	75	40.0
130	50	S-B	100	20.2*
12	30	S-B	100	20.1
21	10	S-B	100	25.2
G-13		Buna 115	100	40.3
CKG-666P		Russian polybutadiene	100	41.6
G-1		GR-S	80†	19.2
RD-27	50	Emulsion polybutadiene	100	20.0

\* All gel removed.

† Estimated.

‡ Ozonization number\* is an expression used to indicate the per cent of 1,2 addition which is determined by ozonolysis of the polymer and subsequent determination of the formic acid. This is not an accurate measure of the per cent of 1,2 addition but it is an approximate value and useful for comparative purposes.

## STYRENE CONTENT

The ratio in which butadiene and styrene enter S-BS at various conversions is apparently much the same. The ratio was determined by means of ultraviolet absorption spectra of polybutadiene, polystyrene, and the copolymer. The specific extinction for 30° C S-B at 260  $m\mu$  is 0.068, compared to 0.039 for emulsion polybutadiene and that for 30° C polystyrene prepared with sodium has a value of 2.20, compared to 2.10 for emulsion polystyrene. Copolymers of butadiene and styrene produced by sodium dispersed under *n*-hexane gave essentially the same absorption as those produced by sodium dispersed under toluene, which indicates that little or no toluene entered the polymer chain. The specific extinction of 50° C S-B is only slightly higher than that of 30° C S-B. Because of this variation in absorption and failure to stop polymerization immediately, the results are somewhat erratic. It is significant that, although the values are slightly high, they show no trend or marked variation with conversion. This behavior is in contrast to that of emulsion copolymerization, which produces polymers containing approximately 17 per cent styrene at low conversions, while at higher conversions the styrene content increases smoothly to a maximum of 25 per cent (Table XIV<sup>10</sup>).

TABLE XIV  
STYRENE CONTENT AS A FUNCTION OF CONVERSION OF 30° C S-BS

Run No.	Conversion (%)	Styrene (%)
336	25	25.2
331	30	26.7
338	30	27.1
388	32	28.2
332	50	28.8
390	57	25.8
389	65	27.2
386	100	26.3
387	100	26.6

*Substituted styrenes.*—Of a series of styrene derivatives which were tested with butadiene at a weight ratio of 25:75 in the sodium formulation, only *m*-methylstyrene gave a promising copolymer in a reasonable length of time. Polymerization was complete in approximately four days at 30°; the rubber was soluble in benzene and had an intrinsic viscosity of 1.5. It was quite soft and tacky, and had the property of cold flow.

Hard, granular, insoluble copolymers were obtained with 1-cyanobutadiene, 2-vinyl-5-ethylpyridine, and 2,5-dichlorostyrene. The last monomer required excess sodium and chloride ion was found in the polymer. Both *p*-dimethylaminostyrene and *p*-methoxystyrene gave very soft copolymers after prolonged rotation; *p*-acetoxystyrene and *m*-nitrostyrene inhibited polymerization completely.

## SUMMARY

1. A convenient laboratory procedure for the sodium-catalyzed copolymerization of butadiene and styrene has been described. Earlier attempts to accomplish this probably failed because the monomers were not sufficiently pure.

2. The copolymer of butadiene and styrene which results from sodium polymerization is different from the emulsion copolymer, GR-S, in several

important respects. The sodium-catalyzed copolymer has a more nearly constant styrene content at different stages of conversion; it is made up of molecules with a relatively narrow molecular weight spread; it has a higher intrinsic viscosity; it is 100 per cent soluble in benzene (*i.e.*, there is no gel) even at 100 per cent conversion; when treated with standard rubber antioxidant, it ages better; and it has a greater amount of the butadiene joined in the 1,2 manner (*i.e.*, greater vinyl side-chain content).

3. The effects of such variables as temperature of polymerization, method of adding the monomer mixture to the catalyst, size of catalyst particles, and possible butadiene impurities on the polymerization have been studied.

4. The method has been extended to cover copolymerization of butadiene and *m*-methylstyrene to give a soluble copolymer of low molecular weight. Other styrene-type monomers gave less interesting copolymers.

#### REFERENCES

- <sup>1</sup> Mathews and Strange, British patent 24,750 (1910); Bayer & Co., British patent 1125 (1911); Harries, *Ann.* **383**, 157 (1911); Perkins, *J. Soc. Chem. Ind.* **31**, 616 (1912).
- <sup>2</sup> Ebert, Heidebrock and Orth, U. S. patent 2,209,746 (1940).
- <sup>3</sup> Koblianskii and Ivanova, *Sintet. Kauchuk* **4**, No. 3, 11 (1935); see *C.A.* **29**, 6799 (1935). These authors found that the polybutadiene near the catalyst rods was only partially soluble.
- <sup>4</sup> See Abkin and Medvedev (*Trans. Faraday Soc.* **32**, 286 (1936)) for the effect of temperature on sodium-catalyzed polymerization of butadiene.
- <sup>5</sup> See Kriuchkov and Shatalov (*Sintet. Kauchuk* **5**, No. 2, 15 (1936); *C.A.* **30**, 4719 (1936)) for the effect of water on sodium-catalyzed butadiene polymerization.
- <sup>6</sup> The data on aging were furnished by F. T. Wall, and will be published in detail elsewhere.
- <sup>7</sup> The molecular-weight data and heterogeneity indices were furnished by F. T. Wall, and will be published in detail elsewhere.
- <sup>8</sup> Ziegler, Grimm and Willer, *Ann.* **542**, 90 (1940).
- <sup>9</sup> These data on the vinyl side-chain content were obtained from Rabjohn, Inskeep, Bryan, Lawson and Johnston, and will be published in further detail elsewhere.
- <sup>10</sup> The data on styrene content were furnished by H. A. Laitinen and T. D. Parks, and will be published in greater detail elsewhere.

# COMPOSITION OF BUTADIENE-STYRENE COPOLYMERS PREPARED BY EMULSION POLYMERIZATION \*

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## INTRODUCTION

The formation of a high-polymer molecule occurs by the successive additions of monomer molecules to a growing chain (chain propagation), the growing chain itself being made up of a number of monomer molecules with a radical derived from a monomer molecule on the end of the chain at which addition occurs. It was pointed out by Norrish and Brookman<sup>1</sup> that chain propagation in the formation of a copolymer from two polymerizing monomers involves four different reactions; the growing chain may have a radical unit derived from either of two monomers at the end of the chain, to which either of two monomer molecules may add. In general it may be expected that the four growth processes will involve four different reaction-rate constants. This situation has been studied thoroughly from the theoretical point of view by Alfrey and Goldfinger<sup>2</sup>, by Mayo and Lewis<sup>3</sup>, by Wall<sup>4</sup>, and by Simha and Branson<sup>5</sup>. The theoretical treatment has been extended by Walling and Briggs<sup>6</sup> to the copolymerization of an arbitrary number of monomers. A considerable amount of experimental data on copolymerizations of various pairs of monomers in homogeneous solution and the quantitative interpretation in terms of the concept given above have been presented<sup>7</sup>. Prior to the comprehensive treatments of the composition of copolymers referred to above<sup>8</sup>, Wall<sup>9</sup> had shown that a relatively simple treatment could be given to the problem, on the assumption that only two rate constants are involved in the chain propagation, corresponding to the addition of either of two monomers to the growing chain. This would mean that both radical types on the end of the growing chain would have the same relative reactivity with monomers. Wall<sup>4</sup> has pointed out that such a copolymerization would be "ideal" in the same sense as a pair of liquids which follows Raoult's law. Mayo and Lewis<sup>3</sup>, however, have stated that this "ideal" copolymerization behavior does not correspond to the experimental facts in the case of the bulk copolymerization of styrene and methyl methacrylate, or in the case of the copolymerization of maleic anhydride with certain ethylene derivatives.

All the experimental work thus far reported<sup>10</sup> has been on copolymerization in homogeneous solutions. It is interesting to investigate the composition of copolymers prepared by emulsion polymerization. In this paper, experimental data are presented on the composition of copolymers of butadiene and styrene prepared by emulsion polymerization over a wide range of conversions from monomer to polymer and wide variations in the proportions of the monomers in the charge, as well as certain variations in the formula and temperature of

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the emulsion polymerization. The interpretation of the data is discussed in terms of the theories referred to above.

### EXPERIMENTAL

All the copolymers were prepared by emulsion polymerization. The temperature of polymerization was 50° C unless otherwise indicated, and the formula used was that referred to previously<sup>11</sup>.

Ingredient	Parts by wt.
Butadiene	Variable
Styrene	Variable
Water	180
Soap	5
Thiol	0.5
Potassium persulfate	0.3

The chemicals used were as follows: butadiene (Carbide and Carbon), purity more than 99 per cent, bubbled through sodium hydroxide and dried over calcium chloride before condensation in dry ice-acetone; styrene (Monsanto), purity at least 99.5 per cent, used without further purification, since separate experiments showed that the same results were obtained with this material as with styrene which had been purified carefully by vacuum distillation; soap (Ivory Flakes), a commercial product containing sodium oleate, stearate, and myristate; thiol, *n*-dodecanethiol or a commercial product of a mixture of thiols of approximately C<sub>12</sub> average molecular weight; potassium persulfate (Merck or Baker's c.p.).

The charges were prepared in 4-oz. glass pressure bottles with metal screw caps with rubber gaskets protected by aluminum caps. In filling a given bottle, the proper amounts of soap solution and persulfate solution were added from pipets, the aqueous phase was cooled to 0° C, the proper amount of styrene was added from a pipet, after which the butadiene, which had been condensed in a dry ice-acetone mixture, was added. To remove air from the gas space above the solution, a slight excess of butadiene was added and the excess allowed to evaporate, after which the bottle was capped and placed in the thermostat (controlled to 0.1° C).

After the proper time of polymerization, the bottles were removed from the thermostat, cooled in ice water, and a small amount (about 0.1 per cent) of hydroquinone or  $\beta$ -naphthol was added. The latices were coagulated in ethanol; the polymers were purified, either by extraction for several hours with ethanol or by precipitation from chloroform solution with ethanol, and dried in a vacuum oven at 50° C. The percentage conversion was determined by evaporation of an aliquot portion of the latex (containing a trace of hydroquinone) at 110° C. Since the residual monomers are volatile at this temperature, the weight of polymer is equal to the weight of solid residue after a correction is applied for the nonvolatile persulfate, soap, and hydroquinone.

The composition of the copolymer was determined in almost every case by the ultraviolet spectrophotometric method which has been described elsewhere<sup>10</sup>. In the case of a few high-conversion polymers, which contained gel, so that the spectrophotometric method could not be applied, the composition was determined indirectly by measuring the amounts of residual monomers by methods which are to be described elsewhere<sup>12</sup>. As is evident from a consideration of the errors involved in the indirect method, it can be applied with fair accuracy only to polymers having a conversion of more than 60–70 per cent.

In a few cases the copolymer compositions were determined also by the iodine chloride method of Kemp and Peters<sup>13</sup>, in the application of which the percentage unsaturation of the copolymer is assumed to be equal to the percentage of butadiene<sup>14</sup>. These methods are considered to have about the same relative accuracy (approximately 3 per cent relative for a copolymer containing about 20 per cent styrene).

The uncertainty in determining the relation between conversion and composition is due not only to the uncertainty in the composition determination on a given copolymer but also to the lack of reproducibility in the preparation of the copolymers. The butadiene must be added as a condensed gas, at a temperature not far below its boiling point of  $-5^{\circ}\text{C}$ . This makes it difficult to reproduce the weight of butadiene more closely than a few tenths of a gram, out of a total quantity of about 10 to 30 grams. Since the polymerizations are carried out in glass bottles with metal screw caps, and the pressure in the bottle at  $50^{\circ}\text{C}$  is almost 5 atmospheres with 75 parts of butadiene in the charge, a slight amount of leakage is almost inevitable during the course of the polymerization. In general, the precision (judged by the reproducibility of the results obtained with different polymerizations under presumably identical conditions) and the accuracy (judged by the agreement of independent analytical methods) appear to be about 4 per cent (relative). This estimate may be used in considering the composition data presented in this paper.

#### EXPERIMENTAL

The relation between composition and conversion for butadiene-styrene copolymers prepared by emulsion polymerization at  $50^{\circ}\text{C}$  according to the previously cited formulation with 75 butadiene: 25 styrene (parts by weight) in the charge is given in Figure 1. It is evident that the experimental data can be represented by a smooth curve rising from about 17.2 per cent styrene in the first polymer formed (at 0 per cent conversion) to 25 per cent styrene at 100 per cent conversion. The latter figure corresponds to the fact that the overall composition of the copolymer at 100 per cent polymerization must be identical to the composition of the monomers in the original charge. Values of the percentage of styrene in the copolymer at various conversions, taken from the smooth curve of Figure 1, are given in Table I.

TABLE I  
WEIGHT PERCENTAGE OF STYRENE IN BUTADIENE-STYRENE COPOLYMERS PREPARED  
IN EMULSION, WITH 25 PER CENT STYRENE IN THE CHARGE

Conversion (percentage)	Styrene (percentage)
0	17.2
20	17.9
40	18.7
60	19.7
80	21.2
100	25.0

Similar composition-conversion data for other monomer ratios (from butadiene:styrene = 87.5:12.5 to 12.5:87.5) in the charge are presented in Figure 2. Although the experimental data are less numerous than those presented in Figure 1, it is evident that the variation of composition with conversion can be represented by a smooth curve, rising from a value which corresponds to an



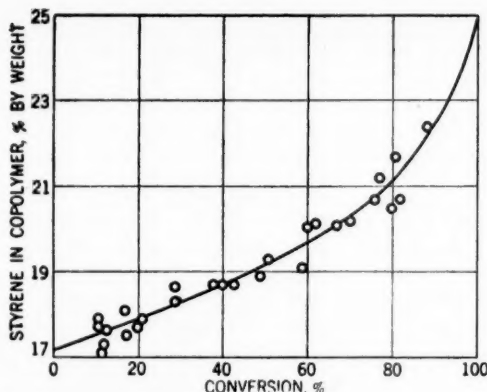


Fig. 1.—Styrene content of butadiene-styrene emulsion copolymers as a function of conversion. Styrene in the charge, 25 per cent by weight.

amount of styrene in the copolymer less than that which is present in the original charge, to this latter value at 100 per cent conversion.

In addition to the polymerizations at 50° C, a few polymerizations were carried out at 30° and at 70°, using the previously quoted formula with the monomer ratio, butadiene:styrene = 75:25 (by weight). The data indicate that variation of the temperature of polymerization (in the range of 30° to 70° C) does not affect the copolymer composition, within the limits of experimental error (approximately 1 per cent absolute).

Composition determinations were made also on copolymers prepared from a charge containing butadiene:styrene = 75:25, with the previously quoted formulation modified with respect to the amount of soap, the amount of thiol, and the kind of catalyst. The amount of soap was varied from one to one-sixteenth times the normal amount, the amount of thiol from one to four times the normal amount, and potassium persulfate was replaced by another water-

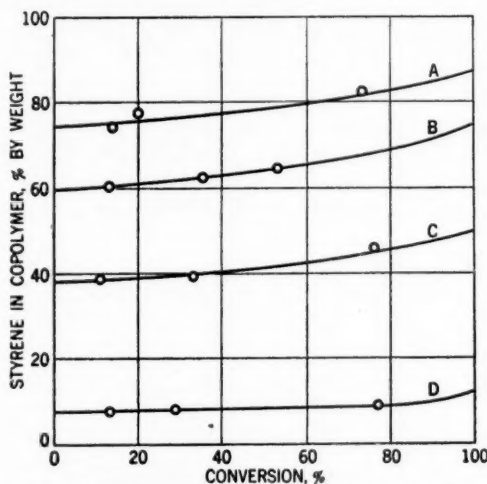


Fig. 2.—Styrene content of butadiene-styrene emulsion copolymers as a function of conversion. Styrene in the charge, percentage by weight: A, 87.5; B, 75; C, 50; D, 12.5.

soluble catalyst. None of the variations caused any change in the composition of the copolymer produced at a given degree of conversion. This observation is in agreement with the result reported by Mayo and Lewis<sup>15</sup> that the composition of styrene-methyl methacrylate copolymer at a given conversion is not affected by the presence or absence of the catalyst, benzoyl peroxide, or by the addition of ethylbenzene, water, dodecanethiol, benzene, or ethyl acetate.

### DISCUSSION

Figures 1 and 2 show that the copolymer formed at the start of the reaction contains relatively more butadiene than is present in the charge. This means that butadiene enters the copolymer relatively more rapidly than does styrene. As the reaction continues, the amount of residual butadiene decreases relatively more rapidly than does the amount of residual styrene, so the percentage of styrene in the copolymer increases with increasing conversion.

The quantitative interpretation of the data obtained in an emulsion copolymerization (compared to copolymerization in a homogeneous phase) is made uncertain by the fact that one does not know the concentrations of monomers at the locus of the propagation reaction during all the stages of the copolymerization. During approximately the first half of the reaction, the monomers exist as a separate phase, since the solubility of both butadiene and styrene in water or in aqueous soap solutions is relatively small (far less than 100 parts of hydrocarbon in 180 parts of water). However, copolymerization does not occur in the hydrocarbon phase, but in the aqueous phase; experimental data are not yet available on the solubilities of both butadiene and styrene in aqueous soap solutions. (It may be pointed out that the concentrations existing during the copolymerization need not correspond necessarily to their equilibrium values.) Even during the latter part of the copolymerization, after the separate hydrocarbon phase has disappeared and the residual monomers are dissolved in the polymer particles in the latex, the monomer concentrations are still unknown; however, in this case the ratio of the monomer concentrations must necessarily be the same as the ratio of the amounts of unreacted monomers. (Only a relatively small amount of either monomer dissolves in pure water.) Assuming that only one molecule of monomer is involved in the propagation reaction, *i.e.*, that only one molecule at a time adds to the growing chain (and this assumption may be regarded as a virtual certainty), the propagation reaction is first order with respect to the monomer; this, of course, does not mean that the overall reaction rate must be first order with respect to the monomer. Thus the ratio of the monomer concentrations is sufficient to define the composition of the copolymer. During the first half of the reaction, however, even the ratio of concentrations at the locus of the propagation reaction is unknown.

Let us make the assumption, the consequences of which will be discussed, that the ratio of concentrations at the propagation locus is equal to the ratio of the amounts of monomers present at any given conversion. If the copolymerization is assumed to be ideal, the rate of disappearance of each monomer is given by the equations:

$$-dB/dt = k_B BR \quad (1)$$

$$-dS/dt = k_S SR \quad (2)$$

in which *B* and *S* refer to concentrations (proportional to amounts, see preceding discussion) of residual butadiene and styrene, and *R* is the concentration of

the growing polymer chain to which each monomer adds. In this preliminary calculation a given monomer is assumed to react equally rapidly with radicals derived from different monomer molecules at the end of the growing polymer chain. The concentration of the radical,  $R$ , at the locus of the propagation reaction depends on the amounts and natures of the catalyst, emulsifier, and thiol, as well as on the monomers themselves. It has been emphasized by Mayo and Lewis<sup>15</sup> and others that composition data alone cannot yield any information as to the magnitude of  $R$ .

From Equations (1) and (2), we obtain:

$$dB/dS = \alpha(B/S) \quad (3)$$

in which the new constant,  $\alpha$ , is the ratio of the propagation reaction rate constants of  $B$  and  $S$ ; this is the *alpha coefficient* introduced by Wall<sup>16</sup>. As a consequence of the assumption above, the ratio of monomer concentrations can be replaced by the ratio of amounts of monomers. The following symbols are defined:  $B_0$  and  $S_0$  are the original amounts of butadiene and styrene, respectively, in the charge;  $B$  and  $S$ , the amount of butadiene and styrene, respectively, unpolymerized at any conversion;  $B_P$  and  $S_P$ , the amount of butadiene and styrene, respectively, polymerized at any conversion;  $R$ , the ratio of monomers in the charge,  $B_0/S_0$ ;  $C$ , the degree of conversion of monomer to polymer;  $F_S$ , the fraction of styrene in the entire polymer formed up to any conversion; and  $f_s$ , the fraction of styrene in the polymer increment at any conversion.

The following relations are obvious:

$$\begin{aligned} B_0 &= B + B_P & S_0 &= S + S_P & C &= \frac{B_P + S_P}{B_0 + S_0} \\ F_S &= \frac{S_P}{B_P + S_P} = \frac{S_P}{C(B_0 + S_0)} \\ f_s &= \frac{dS_P}{dS_P + dB_P} = \frac{dS}{dS + dB} \end{aligned} \quad (4)$$

From relation (3) it follows that:

$$B/B_0 = (S/S_0)^\alpha \quad (5)$$

Since  $\alpha$  in general is nonintegral, a relation between  $F_S$  and  $C$  is obtained which cannot be solved explicitly. For purposes of numerical calculation it is convenient to introduce a parameter,  $x$ :

$$x = S/S_0 (0 \leq x \leq 1) \quad (6)$$

which permits the calculation of  $F_S$  and  $C$  for any assigned value of  $x$ :

$$F_S = \left\{ 1 + R \frac{1 - x^\alpha}{1 - x} \right\}^{-1} \quad C = \frac{1 - x}{1 + R F_S} \quad (7)$$

$\alpha$  may be evaluated from the composition of the polymer increment formed at  $C = 0$  (found by extrapolation of experimental data):

$$\alpha = \frac{1}{R} \left( \frac{1}{F_S} - 1 \right) \quad \text{for} \quad C = 0 \quad (8)$$

By extrapolation of the data of Figure 1, it is found that the first polymer increment formed contains 17.2 per cent styrene if the butadiene:styrene ratio in the charge is 75:25 ( $R = 3$ ). This corresponds to the value,  $\alpha = 1.60$ .

With this value of  $\alpha$  the complete composition-conversion curves have been calculated according to Equations (7) for butadiene-styrene ratios of 87.5:12.5, 75:25, and 50:50 ( $R = 7, 3$ , and 1, respectively). The results are given in Table II and Figure 3.

TABLE II  
COPOLYMER COMPOSITION AT VARIOUS CONVERSIONS\*

Conversion (percentage)	Styrene in polymer (percentage)		
	Butadiene:styrene in charge		
	87.5:12.5	75:25	50:50
0	8.2	(17.2)	38.4
20	8.5	17.9	39.7
40	9.0	18.7	41.1
60	9.5	19.7	42.8
80	10.3	21.2	45.4
90	11.0	22.5	47.2
100	(12.5)	(25.0)	(50.0)

\* Calculated on the basis of a reaction which is first order with respect to the monomers;  $\alpha = 1.60$ .

A comparison of the values for  $R = 3$  in Table I (observed values) and Table II (calculated values) shows that the agreement is excellent with this value of  $R$  (see also Figure 3). Figure 3 shows that the agreement of observed and calculated values is fairly good with  $R = 7$  and  $R = 1$ . The agreement with other values of  $R$  will be considered later. In agreement with expectation, the data definitely exclude the possibility that the propagation reaction is second order with respect to the monomers.

An alternate method of calculation of  $\alpha$  may be considered, which introduces the concept of the composition of polymer increments.

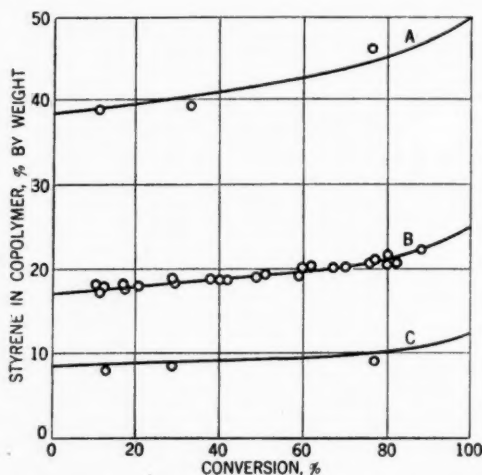


FIG. 3.—Composition-conversion curves of butadiene-styrene emulsion copolymers. The circles are experimental points. The curves are calculated on the basis of the Ideal Copolymerization Theory with  $\alpha = 1.60$ . Styrene in the charge, per cent by weight; A, 50; B, 25; C, 12.5.

The relation between  $f_s$  (styrene content of polymer increment, or "instantaneous styrene content") and  $F_s$  (overall styrene content) is given by the equation:

$$f_s = F_s + C(dF_s/dC) \quad (9)$$

which is a special case of the general relations given by Wall<sup>17</sup>. If  $dF_s/dC$  is evaluated by graphic means,  $f_s$  may be calculated. The ratio of the monomers in the polymer increment is obtained directly from  $f_s$ : hence,  $\alpha$  may be calculated if the ratio of residual monomers is known; this is obtained by stoichiometry.

EXAMPLE: At 50 per cent conversion a smooth curve through the experimental points gives  $F_s = 0.192$ .  $dF_s/dC$  is found by graphic means to be 0.052. Hence  $f_s = 0.192 + 0.50 \times 0.052 = 0.218$ . The corresponding instantaneous butadiene:styrene ratio in the copolymer is  $0.782/0.218 = 3.59$ . The ratio of residual monomers is calculated as follows: if 100 parts of monomers were present originally (75 of butadiene, 25 of styrene), 50 parts of polymer have been formed containing  $50 \times 0.192 = 9.6$  parts of styrene and 40.4 parts of butadiene. Therefore,  $75 - 40.4 = 34.6$  parts of butadiene, and  $25 - 9.6 = 15.4$  parts of styrene are left, corresponding to the ratio  $34.6/15.4 = 2.25$ . Hence,  $\alpha = 3.59/2.25 = 1.60$ , which agrees exactly, by chance, with the value computed at 0 per cent conversion.

Various values of  $\alpha$  have been calculated by such means from the smooth curve drawn through the experimental points. The average value of  $\alpha$  found in this way is  $1.61 \pm 0.01$ .

The composition of the polymer increment formed at any conversion may be calculated from Equations (4), (5), and (8). The result is:

$$f_s = \left[ 1 + \frac{\alpha}{x} \left\{ R - C(1 + R)(1 - F_s) \right\} \right]^{-1} \quad (10)$$

which when applied to the 75:25 ratio, with the known value of  $\alpha$  leads to:

$$f_s = \left[ 1 + \frac{1.60}{x} \left\{ 3 - 4C(1 - F_s) \right\} \right]^{-1} \quad (11)$$

Results obtained from this calculation (which agree with those obtained by graphic means) are given in Table III and Figure 4.

TABLE III  
COMPOSITION OF POLYMER INCREMENTS FORMED AT  
VARIOUS DEGREES OF CONVERSION\*

Conversion (percentage)	Styrene content (percentage)
0	17.2
20	18.8
40	20.6
60	23.3
80	29.5
90	36.4

\* Charging ratio = 75:25.

It was seen from Figure 3 that the agreement of the experimental and calculated values of copolymer composition is excellent for  $R = 3$ , and reasonably good for  $R = 7$  and  $R = 1$ . A calculation according to Equation (7) can be carried out for values of  $R$  less than unity (corresponding to more than

50 per cent styrene in the charge) to test the reliability of the calculated values. An adequate test, however, is provided by examination of the data on the composition of the first increment of copolymer formed. If the simple theory used thus far is applicable, the ratio of the monomers in the copolymer must be proportional to the ratio of the monomers in the charge—overall ranges of compositions.

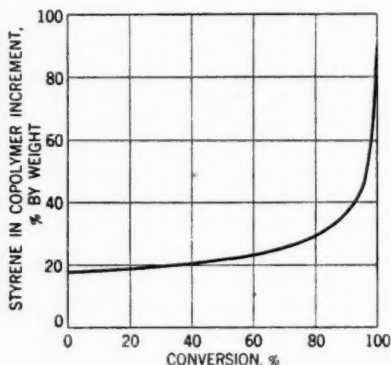


Fig. 4.—Composition of copolymer increments as a function of conversion of a butadiene-styrene emulsion copolymer. Styrene in the charge, 25 per cent by weight.

Accordingly, the curves of Figure 2 were extrapolated to 0 per cent conversion. From these data the monomer ratios in the copolymers were calculated; the quotient of this ratio divided by the ratio of the monomers in the charge is denoted in Table IV as  $\alpha$ , which would be constant if the ideal copolymerization theory were adequate.

TABLE IV  
COMPARISON OF MONOMER RATIO IN THE COPOLYMER WITH  
MONOMER RATIO IN THE CHARGE

Styrene in charge (%)	Styrene in copolymer (%)	$dB/dS$	$B/S$	$\alpha$
87.5	75	0.33	0.143	2.3
75	60	0.67	0.333	2.0
50	38	1.63	1.00	1.63
25	17.2	4.81	3.00	1.60
12.5	7.8	11.8	7.00	1.69

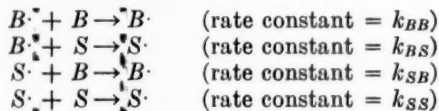
It may be noted that a relatively small uncertainty in percentage composition causes a relatively large uncertainty in the monomer ratio in the copolymer, if this ratio is very much different from unity. For example, if the extrapolated value of the percentage of styrene is  $75\% \pm 3\%$ , the corresponding monomer ratio is  $0.33 \pm 0.05$ .

It is evident from Table IV that the predictions of the ideal copolymerization theory do not agree with the experimental facts if the monomer ratio in the charge is varied widely. This statement applies even in cases in which the uncertainty in the monomer ratio is relatively large (when the ratio is much smaller or larger than unity). Thus, the percentages of styrene in the first polymer increment, calculated with  $\alpha = 1.60$ , are 81.5 and 65.1 per cent respectively, compared to the experimental values of 75 and 60 per cent



respectively, for  $R = 1/7$  and  $R = 1/3$ . These differences appear to exceed the probable experimental error.

It is interesting to see whether the predictions of the exact copolymerization theory are in agreement with the facts. The four possible propagation reactions referred to can be written as:



in which  $B\cdot$  and  $S\cdot$  refer to the growing polymer chain with a radical derived from a butadiene or a styrene molecule, respectively, on the end to which addition occurs. On the assumption that a steady state with respect to free-radical concentration exists, it can be derived<sup>18</sup> that:

$$\frac{dB}{dS} = \frac{B \sigma B + S}{S B + \mu S} \quad (12)$$

in which  $\sigma = k_{BB}/k_{BS}$  and  $\mu = k_{SS}/k_{SB}$ . If  $\mu = 1/\sigma$ , that is, if the monomers have the same relative preference for either radical, Equation (12) is identical with Equation (3) and the alpha concept is valid with  $\sigma = \alpha$ . If  $B/S$  in Equation (12) is replaced by  $R$ , and the experimental value of  $\alpha$  from Table IV is substituted for  $\frac{dB/dS}{B/S}$ , we obtained the equation:

$$\sigma = \frac{\alpha}{R} \mu + \left( \alpha - \frac{1}{R} \right) \quad (13)$$

A single composition determination, therefore, determines a straight-line relationship between  $\sigma$  and  $\mu$ ; the unique values of the constants are found to be the intersection of any pair of straight lines. With perfect experimental data, all the lines would have the same intersection if the theory were obeyed exactly.

When this procedure is carried out with the data of Table IV, it is found that no unique pair of values of  $\sigma$  and  $\mu$  can be determined which are valid for the range  $R = 7$  to  $1/7$ . The most reliable data (those derived from values of  $dB/dS$  not far from unity) lead to values of  $\sigma$  from 1.2 to 1.6, and of  $\mu$  from 0.4 to 0.6, although it must be emphasized that these values are not established exactly. Nevertheless, since  $\sigma$  and  $\mu^{-1}$  are both greater than unity, one may conclude that the reactivity of butadiene with either radical is greater than the reactivity of styrene.

The objection may be raised to the foregoing calculation that it is based on the assumption that the ratio of monomer concentrations at the locus of the propagation reaction is the same as the ratio of the total amounts. This is an assumption that can be checked experimentally by determining the composition of butadiene-styrene copolymers produced in a homogeneous phase. If the concentration ratio is not equal to the amount ratio, then the values of  $\sigma$  and  $\mu$  evidently have to be corrected by a factor, the magnitude of which is given by the ratio of the true monomer concentrations to the amounts. It is interesting to note that, if the copolymerization theory were followed exactly and equilibrium with respect to distribution were attained, unique values of the constants,  $\sigma$  and  $\mu$ , would be found, although these would not correspond to the values which would be found by copolymerization in a homogeneous phase. If distribution equilibrium were not attained, however, unique values

of  $\sigma$  and  $\mu$  would not be found which are valid over a wide range of monomers ratios in the charge.

This can be demonstrated readily if it is assumed that the monomers are dissolved to different extents in the locus of the propagation reaction but that distribution equilibrium is attained. The true ratio of concentrations is then equal to the ratio of the amounts multiplied by a factor which is the ratio of the distribution coefficients. If this is substituted in Equation (12), an equation of exactly the same form results, with the true constants,  $\sigma$  and  $\mu$ , changed by the same factor.

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## GR-S EMULSIFIED WITH ROSIN SOAP \*

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One of the most troublesome deficiencies of standard GR-S, in so far as product fabrication is concerned, is the inherent lack of tackiness or the incapability of laminated and spliced surfaces to flow and knit together easily. This was especially bothersome from 1942 to 1944, when the scarcity of natural rubber forced fabricators to use a synthetic polymer before they had developed satisfactory methods and equipment to compensate for its deficiencies.

Early in 1942, in anticipation of a later scarcity of fats and oils suitable for making the soap used for emulsification, the several groups working on polymer development problems intensified their efforts to find emulsifying agents which could be made from noncritical domestic materials. Rosin was one of these. Early attempts to use it were unsuccessful, however, because the polymerization reaction was strongly retarded. Later the Hercules Powder Company and The B. F. Goodrich Company, working together, found that the retarding effect could be greatly reduced with the use of disproportionated rosin previously referred to as dehydrogenated rosin. (The treatment given to the rosin results in a molecular disproportionation of the hydrogen, with the elimination of the conjugated double bonds accountable for much of the inhibiting effect on the polymerization reaction.) This work made rosin available for use in the event of an actual scarcity of fats and oils of good quality.

Later that year the U. S. Rubber Company discovered that polymer made with disproportionated rosin soap showed considerable promise for alleviating fabricating difficulties because of its higher inherent tackiness. In this respect it was considerably better than polymer made with fat acid soap to which an equivalent amount of either rosin or modified rosin was added in compounding, and slightly better than alkali-extracted fat acid polymer in which the extracted fat acid was replaced with rosin. Of equal importance was the discovery that the disproportionated rosin soap polymer showed superiority in hysteresis, in carcass flexing life, and in resistance to heat build-up, without sacrifice of other important properties.

Concurrently with these compounding and performance evaluations, both the preparation of the rosin and the development of the polymerization formula for using it were diligently investigated by the technical groups of Hattiesburg and Naugatuck, working together and aided by the tire plant. Nearly a year of active, coöperative effort was required to eliminate the difficulties and variations in quality which were experienced in expanding the scale of operations from laboratory to semiplant size. This effort reached its first goal in June, 1943, when the Naugatuck plant made the first production run of X-10

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GR-S. This was followed by a second run in August, a third in September, and one in each succeeding month. A production total of 404,800 pounds was achieved during the first twelve-month period.

Since that time the facilities for making disproportionated rosin have been expanded and the production of polymer has been taken up by the plants at Louisville, Kentucky, Institute, West Virginia, Port Neches, Texas, and Torrence, California; the quality of the modified rosin soap has improved to the point of being more uniform than fat acid soap, as indicated by the uniformity of the polymerization reaction. Production of general purpose rosin polymer GR-S 10 now (March, 1946) totals approximately 16,000,000 pounds per month, or a little more than one seventh of the total GR-S polymer production. Types of rosin polymer in production at the present time are given in Table I.

TABLE I  
TYPES OF ROSIN POLYMERS (76.5% BUTADIENE-23.5% STYRENE)  
IN PRODUCTION

Designation	Mooney viscosity	Contained stabilizer
GR-S 10	55	1.5% PBNA or BLE <sup>a</sup>
X-273 GR-S	55	1.5% exptl. antioxidant 401 <sup>b</sup>
X-272 GR-S	100	1.0% Stalite <sup>c</sup>

<sup>a</sup> Phenyl- $\beta$ -naphthylamine or acetone-diphenylamine reaction product.

<sup>b</sup> Phenol-phosphorus trichloride reaction product.

<sup>c</sup> Heptene-diphenylamine reaction product.

#### GR-S 10

GR-S 10 differs very little from the X-10 GR-S made in June, 1943, although a good many variations have been made and evaluated in tire tread and carcass compounds during the intervening three years. The advantages to be realized from its use are as follows:

*Increased Banbury Output (20 per cent) through Use of Concentrated Master Batches.*—This method of compounding was not possible with standard GR-S because the master batches were dry and crumbly and not so easy to handle on the Banbury mill.

*Better Adhesion of Calender Coat to Solutioned Fabric before Vulcanization.*—This enabled tire factories to increase calender efficiency 10–15 per cent by permitting skim and friction coating at higher speed. It also reduced “peeling” of the calender coat in the cutting and building operations and, as a result, reduced fabric scrap and product building labor. In addition it reduced the number of raw tires to be repaired because of separation occurring during the tire-shaping operation.

*Greater Tackiness for Laminating and Splicing, Particularly for Compounds Containing Some Natural Rubber.*—The addition of a small quantity of natural rubber to GR-S 10 compounds enhances the tackiness for fabricating purposes to a greater extent than does an equivalent addition to corresponding standard GR-S compounds.

*Better Ply-Separation Resistance.*—The much improved resistance to ply-separation of GR-S 10 carcass compounds is indicated by the rating given in Table II for an indoor wheel test made by our Detroit tire plant. This is typical of the results obtained by several performance evaluations, both indoor and highway.

*Higher Heat-Break Resistance.*—The improvement in heat-break resistance realized from the replacement of standard GR-S with GR-S 10 in carcass compounds is about 25 per cent (Table II).

*Possibly Better Abrasion and Cut-Growth Resistance.*—The results of road tests completed to date have been inconclusive; additional tests are being made to fix these points.

TABLE II  
INDOOR WHEEL TEST (DETROIT PROJECT 8540)

Elastomer in carcass	Standard GR-S	GR-S 10
Ply-separation rating	100	156
Heat-break rating	100	126

The disadvantages are few and are easily offset by minor changes in compounding and processing. The four differences requiring consideration follow:

*More Viscous than Standard GR-S.*—The viscosity to which GR-S 10 is made is the result of a compromise between the desire for performance quality and the need for processibility. GR-S 10 as currently made requires slightly more mastication than standard GR-S to obtain the same processibility.

*Slightly More "Scorchy".*—If part or all of the greater mastication requirement is denied, processing temperatures are higher and the tendency for scorching is increased. If production schedules permit part of the saving in Banbury and mill time realized from the use of concentrated master batches to be applied to polymer mastication, the compounds should be as safe as those made with standard GR-S.

*Slower Curing than Standard GR-S.*—The difference in rate of vulcanization can be corrected by an adjustment of the accelerator ratio and the addition of 1.0 to 1.5 parts of fat acid.

*Tendency to Stick on Mill and Calender.*—This can be overcome by the use of standard GR-S or natural rubber as part of the elastomer in the compound. The addition of 1.0 to 1.5 parts of fatty acid is generally sufficient to correct for this tendency. If natural rubber is used as part of the elastomer in the compound, no sticking should be experienced.

Although emphasis has been placed on the performance of GR-S 10 in tire compounds, its value is not limited to tires. It offers advantages in the compounding of many products, such as hoses, shoe soles, power transmission and conveyor belts, etc., in which nonblack fillers or low loadings of black fillers must be used to obtain required appearance or performance characteristics.

In hose friction compounds it gives the advantage of easier calendering and greater tackiness for product building. Performance quality is equal to or slightly better than that of corresponding standard GR-S compounds. Our mechanical goods plant has realized a saving of as much as 18 per cent in the building time of suction and fire hoses through the use of rosin polymer.

In shoe soling it offers the advantage of slightly better abrasion resistance and higher tensile strength, without sacrifice of resilience, tear resistance, or other important cured properties.

In power transmission and conveyor beltings the replacement of standard GR-S with GR-S 10 would increase calendering efficiency, improve service life, particularly in high speed applications.

#### X-273 GR-S

X-273 GR-S is a nondiscoloring, nonstaining variation of GR-S 10; it is specially made for use in white and light-colored compounds which are required



to retain their brilliance throughout life, and for all compounds which are required to be free from the tendency to stain paper, paint, enamel, or lacquer surfaces with which they may come in contact during service.

Its similarity to GR-S 10 in properties and freedom from discoloring and staining tendencies indicates advantage in the compounding of white shoe soles and heels, mottled floor tile, light-colored electric lamp cord, and white sidewall tires. This is a relatively new variation, and as yet the production of this polymer is low in volume; but it is expected to increase when the evaluations now in progress have been completed.

#### X-272 GR-S

Rosin polymer is also available in a third form under the Rubber Reserve designation, X-272 GR-S. This modification made its first appearance as X-40 GR-S on December 28, 1943, when the Naugatuck polymer plant completed the production of two batches. Since that time 1,132,000 pounds have been produced for use in the compounding of adhesives and pressure-sensitive tapes. In these applications X-272 GR-S is definitely superior to standard GR-S and its variations.

*Much Higher Raw Strength.*—High raw strength or cohesiveness is necessary to prevent transfer to the adhesive from one surface to another, and to give bonds which do not break when subjected to continuous low stresses.

*No Fat Acid Content to Crystallize Internally or Bloom to Surface.*—Since surface tackiness and the performance quality of the product are reduced by crystallization and blooming, this is a matter of much concern to tape and adhesives manufacturers.

*Nondiscoloring Tendency.*—The stabilizer in X-272 GR-S is low in discoloring tendency and does not darken appreciably during exposure to light. This is of importance in transparent-back tapes, stationery adhesives, etc.

*Low in Water-Soluble Substances.*—This is an important consideration in tapes made for electrical applications in which the adhesive is in contact metal surfaces. X-272 GR-S is low in soluble soap and ash which would cause corrosion.

X-272 is slightly less soluble in common solvents than Standard GR-S or GR-S 10, but its solubility is sufficient to permit processing in the normal manner.

#### ACKNOWLEDGMENT

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## THE MECHANISM OF MODIFIER ACTION IN THE GR-S POLYMERIZATION. I\*

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When butadiene and styrene are copolymerized in an aqueous emulsion containing only the monomers, an emulsifying agent, and a peroxidic catalyst, the product obtained is an insoluble substance which is difficult to process and is of little value as a rubber. Useful copolymers are obtained by adding to the polymerization system a substance known as a "modifier". In the preparation of GR-S, the modifier used is a thiol or a mixture of thiols. The copolymer produced in the presence of such a modifier is soluble in benzene, and it can be milled and processed much like natural rubber. The present work was undertaken in an effort to determine the nature of the chemical action of the modifier.

It is now generally believed that vinyl polymerizations induced by peroxidic catalysts proceed by a free radical mechanism<sup>1</sup> in which the essential steps are initiation, propagation, and termination. Peroxide-catalyzed polymerizations of dienes differ from those of simple vinyl monomers in that the steps of initiation and propagation may consist in either 1,4- or 1,2-addition to the diene system, or both 1,4- and 1,2-addition may occur in random fashion. Ozonization studies of polybutadiene indicate that the polymer has a structure of the third type, resulting from both 1,4- and 1,2-addition<sup>2</sup>.

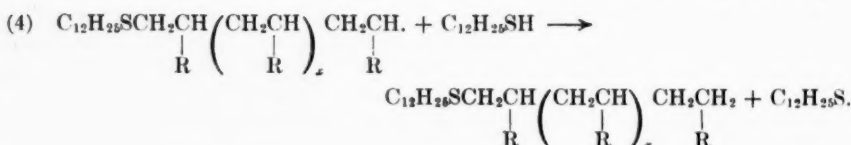
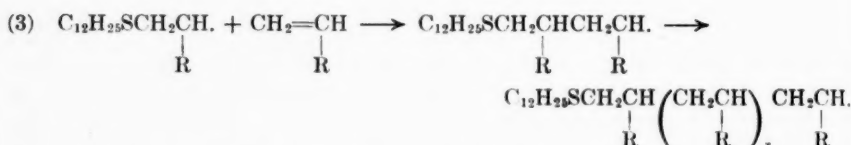
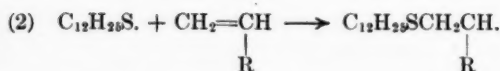
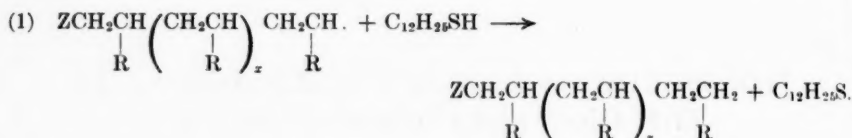
At the time of the beginning of the present work two theories were under general discussion as providing possible explanations for the action of modifying agents. In one it was supposed that the modifier acted as a catalyst for 1,4-addition to the diene, or as an inhibitor for 1,2-addition, so that its use resulted in the formation of polymer of essentially linear structure. In the absence of a modifier the polymerization was supposed to yield a product in which a large proportion of the diene units were combined as 1,3-butadiene residues

$$\left( \begin{array}{c} -\text{CH}_2\text{CH}- \\ | \\ \text{CH}=\text{CH}_2 \end{array} \right).$$
 The side-chain vinyl groups in this structure were supposed to be more reactive than the internal double bonds of the structure resulting from 1,4-addition. For example, the side-chain vinyl groups were supposed capable of participation in the polymerization reaction, leading to branched and cross-linked molecules.

In the second theory<sup>3</sup>, it was supposed that the modifier acted as a chain-transfer agent. For example, a molecule of *n*-dodecanethiol may react with one polymer radical to stop its growth, but producing a radical which may start

\* Reprinted from the *Journal of the American Chemical Society*, Vol. 68, No. 8, pages 1422-1428, August 1946. This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government synthetic rubber program.

the growth of another. The following equations represent such a chain-transfer process:



Kharasch, Read and Mayo have demonstrated that reactions of the type represented by Equation 2 occur<sup>4</sup>.

According to this theory, the function of the modifier is to regulate the molecular weight of the polymer. It is possible that it also has an effect on cross-linking, however. For example, in the absence of a chain terminator a reactive polymer radical may add to a double bond in another such radical or molecule, so that the attacked body becomes activated at an internal position, and on further growth yields a cross-linked molecule.

Consideration of the theories and of the equations (1-4) suggests several approaches to experimental tests concerning the mechanism of modifier action. In the first place, if the modifying agent functions by regulating the ratio of 1,4- and 1,2-addition, then it should have no effect on the polymerization of styrene. However, if the agent acts by the chain-transfer process, then successively increasing amounts of modifier should lead to polystyrenes of successively lower molecular weight. The same general effect of modifier concentration on molecular weight should be observed with butadiene polymers and styrene-butadiene copolymers. Furthermore, according to the chain-transfer theory the group RS- appears in each polymer molecule, except those in which the initiation step involved a radical from the catalyst. If this formulation of the mechanism is correct, then the polymer should contain very nearly one sulfur atom per molecule.

## EXPERIMENTAL

### A. POLYSTYRENE

1. *Bulk Polymerization.*—The catalyst, 0.5 g. of benzoyl peroxide, was dissolved in 20 g. of styrene; *n*-dodecanethiol, in amounts varying from 0.1 to 5 g., was added to this mixture in a small Erlenmeyer flask. The flask was

then stoppered with a tin-foil wrapped cork and heated in an oven at 60–75° for about twenty hours. At the end of this time, 0.5 g. of hydroquinone was added as shortstopping agent to prevent further polymerization; the mixture was transferred and treated with steam to remove the excess styrene. The polystyrene was then washed well with methanol.

Purification of the polymer was effected by reprecipitation by dropwise addition of a dioxane solution of the polystyrene to a vigorously stirred excess of methanol. Three precipitations were made with each sample. Careful drying of the purified product in a vacuum-drying pistol gave a fine white powder.

**2. Emulsion Polymerization.**—A 2.5 per cent aqueous solution of Ivory soap flakes was used as a stock emulsifying solution. To a 4-ounce bottle was added 20 g. of the 2.5 per cent dodecanethiol, which varied in amount from 0.05 g. to 8 g., was dissolved in 10 g. of styrene, and the mixture was added to the polymerization bottle. The bottle was sealed with a screw cap fitted with a tin-foil gasket. The polymerization was carried out by tumbling the bottle in a constant temperature water-bath at 50° for about twenty hours.

After removal of the bottle from the bath, 0.5 g. of hydroquinone was added as a shortstopping agent, and the latex was coagulated in a beaker by means of a saturated sodium chloride solution containing a little sulfuric acid. The sticky polymer was subjected to steam distillation to remove excess styrene and then washed well with methanol. Reprecipitation was effected by dropwise addition of a dioxane solution of the polymer to an excess of methanol. Fine white powders or fibers were obtained after drying in a vacuum pistol.

TABLE I  
BULK POLYMERIZATION OF STYRENE WITH *n*-DODECANETHIOL AS MODIFIER

Run	Styrene (g.)	Dodecanethiol (g.)	Benzoyl peroxide (g.)	Temp. (° C)	Time (hours)	Conversion (%)	Sulfur content (%)	Molecular weight (viscosity)	Molecular weight cryoscopic	S/mole
1	10	0.05	0.1	90–100	15	80				
2	10	.10	.1	90–100	15	70				
3	10	.20	.1	90–100	15	66		17,950		
4	10	.40	.1	90–100	15	60		10,400		
5	15	.85	.85	60	30	60		9,100		
6	20	1.50	.50	60	22	49.5				
7	10	0.80	.80	65	22	40		5,000		
8	10	2.0	2.0	65	22	31.5	5.0–5.5	1,290	920	1.6
9	20	3.5	2.5	65	24	36.4	3.5–3.6	4,000	1100	1.2
10	20	4.2	0.5	60	21	34.0	2.8–3.1		1000	0.97
11	20	1.5	.5	60	21	50				
12	20	2.0	.5	60	21	45	1.28	2,550	1700	.7
13	20	2.8	.5	60	21	33(?)	1.99	2,000	1650	1.03
14	20	3.5	.5	60	21	37	2.29	925	1200	.86
15	20	4.2	.5	60	21	33.5				
16	18	2.52	.5	75	17	42.5	1.4–1.75	2500–2700		1.2–1.3
17	18	1.45	.5	75	17	57.5	2–2.75	1500–1700		1.0–1.3
18	8.1	5.6	1.0	65	20		10.64		300	1.0

**3. Molecular Weight Determinations.**—Cryoscopic molecular weights measured on benzene solutions of the low polymers were reproducible within reasonable limits, and are believed to be sufficiently accurate for the present purpose. Viscosity measurements also were made, but less significance is attached to the molecular weights calculated from them. An Ostwald type viscometer was used, and the molecular weights were calculated in accordance with the Kemp-Peters modification<sup>5</sup> of the Staudinger equation.

The results of these molecular weight measurements are given in Tables I and II.

4. *Sulfur Analyses.*—The purified polystyrenes were ground into fine white powders and oxidized by the Parr bomb method. Sulfur analyses were made on the resulting inorganic residues gravimetrically, with precipitation of the sulfur as barium sulfate and weighing as such in the usual manner.

Sulfur analyses on polystyrenes are given in Tables I and II. Comparison of sulfur analyses was made with the cryoscopic values for the molecular weight in all cases where such values were determined.

TABLE II  
EMULSION POLYMERIZATIONS OF STYRENE WITH *n*-DODECANETHIOL AS MODIFIER

Run	Styrene (g.)	Dodecanethiol (g.)	2.5% soap solution (g.)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g.)	Temp. (° C)	Time (hours)	Sulfur content (%)	Molecular weight (viscosity)	Molecular weight (cryoscopic)	Ratio S/mole
1	10	0.05	20	0.03	50	18	..	4400	2800	0.96
2	10	1.00	20	0.50	50	18	1.1	..	1325-1500	.8-0.9
3	10	2.6	20	0.60	50	18	1.82-1.91	..	1647	.94
4	10	2.6	20	0.60	50	22	1.80-1.83	..	12,975	1.1-1.2
5	10	2.6*	20	0.60	50	20	0.3	12,975	12,350	1.1-1.35
6	23	6.0	45	0.80	50	18	2.5-2.95	1200-1500	..	1.0
7	9	5.07	20	1.0	50	22	..	†	..	1.0

\* Added stepwise; 0.01 g. at start, 0.02, 0.04, 0.08, 0.16, 0.32, etc., added each hour. † Addition compound, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>SC<sub>17</sub>H<sub>35</sub>, isolated as main product.

5. *Cleavage of the Modified Polystyrene with Chlorine and Water.*—To a solution of 5 g. of a dodecanethiol modified polystyrene (molecular weight about 1500) in 50 cc. of chloroform was added 3 cc. of glacial acetic acid. Addition of 20 cc. of water caused the formation of a separate layer, and this mixture was saturated with hydrogen chloride gas. Chlorine was next bubbled slowly through the mixture, the flask being shaken vigorously during this addition and cooled externally to keep the reaction mixture near room temperature. After saturation with chlorine had been effected, the chloroform layer was separated from the water, free chlorine and hydrogen chloride were removed from it, and the solution was added dropwise to an excess of methanol. Several reprecipitations of the polymer from dioxane solution were made, and it was then analyzed qualitatively for sulfur and chlorine. Tests for sulfur were negative, but those for chlorine were strongly positive. It appeared that cleavage of the polymer had taken place in accordance with the equation<sup>6</sup>: C<sub>12</sub>H<sub>25</sub>-S polymer + 3Cl<sub>2</sub> + H<sub>2</sub>O → C<sub>12</sub>H<sub>25</sub>SO<sub>2</sub>Cl + polymer-Cl + 4HCl. In addition, some chlorination of the polymer obviously had occurred, judging from the large amount of chlorine present. However, all attempts to isolate any 1-dodecanesulfonyl chloride from the chloroform-methanol solutions were unsuccessful.

Efforts were made to prepare 1-dodecanesulfonamide directly in the reaction mixture, after removal of the free chlorine, by passing gaseous ammonia through the solution. None of the expected sulfonamide could be isolated from the reaction products.

6. *Hydrogenolysis of Polystyrene.*—A modification of the procedure of Mozingo, Wolf, Harris and Folkers<sup>7</sup> for the cleavage of organic sulfides was used. To a solution of 10 g. of polystyrene (modified with dodecanethiol; molecular weight about 2,000) in 250 cc. of cyclohexane or methylcyclohexane, was added about 200 cc. of *n*-butanol, just short of the amount which would produce cloudiness. After 80 g. of Raney nickel catalyst had been introduced, the mixture was refluxed on a steam cone for six to ten hours. The solution



was filtered to remove the nickel and most of the solvent was distilled, leaving a volume of about 100 cc. of solution. This solution was then subjected to steam distillation. The organic layer of the distillate was dried over magnesium sulfate and distilled from a Claisen flask until about 2 cc. remained in the flask. During this time the distillation temperature rose slowly to 117°, the boiling point of *n*-butanol, where it remained constant until near the end of the distillation. The residual 2 cc. of yellow liquid was transferred to a 10-cc. modified Claisen flask and distilled in vacuum. After removal of the remaining *n*-butanol at room temperature, there were obtained a few drops of a colorless liquid, boiling sharply at 72–73° at 8 mm. pressure. The refractive index at 25° was 1.4205. These constants are in close agreement with those reported in the literature for *n*-dodecane (b.p. 90.5° (11 mm.<sup>8</sup>;  $n_D^{25}$  1.41967)<sup>9</sup>.

**7. Neutralization Equivalents of Polystyrene Modified with Thioglycolic Acid.**—A weighed sample (about 0.5 g.) of the polystyrene was dissolved in 20 cc. of benzene. The solution was heated to boiling, 5 cc. of absolute alcohol was added, and the mixture was titrated with 0.02 *N* alcoholic sodium hydroxide with phenolphthalein as the indicator. For the blank correction, a corresponding amount of unmodified polystyrene was titrated in the same way. The alcoholic sodium hydroxide was standardized against aqueous hydrochloric acid, and, to compensate for any possible end-point changes due to the use of anhydrous solvents, was restandardized against recrystallized benzoic acid dissolved in benzene-alcohol solution. The normality factor was found to be identical in aqueous and nonaqueous solvents.

The end-points in these titrations were sharp and duplicate results were readily obtained. Results are given in Table III.

**8. Saponification Equivalents of Polystyrene Modified with Esters of Thioglycolic Acid.**—To saponify completely the ethyl thioglycolate modified polymers, it was necessary to use a high-boiling medium capable of dissolving the polymer. A mixture of equal parts of toluene and *n*-butanol was found to be satisfactory, and the procedure was carried out as follows:

The sodium butoxide-toluene solution, standardized against potassium acid phthalate, was weighed into a 25-cc. glass-stoppered bottle. A 20-g. portion usually was employed, and, the density of the solution having been previously determined, the volume was calculated to the third decimal place. To this solution a 0.5 g. sample of polymer was added, together with a few drops of water. The stopper was wired down and the bottle placed in boiling water for one to two hours. The solution was then transferred to a 125-cc. Erlenmeyer flask, acidified with standard potassium acid phthalate solution, and the excess acid titrated with standard sodium hydroxide solution.

The method is not ideal, since the end-point is poor and titration of the two-phase system is difficult. The sodium salt of the polymer tends to act as a soap and emulsify the toluene-butanol layer. Blank runs were made in each case on unmodified polystyrene samples. The results are given in Table III.

**9. Molecular Weight Determinations and Sulfur Analysis of Polystyrenes Modified with Thioglycolic Acid and its Derivatives.**—For each sample the molecular weight was determined in a number of ways and the values were compared. Molecular weights were first obtained from the neutralization or saponification equivalents. Secondly, molecular weights were calculated from the percentage of sulfur, assuming one sulfur atom present per polymeric molecule. In two cases osmotic pressure measurements<sup>10</sup> were made and the values of molecular weight obtained by this method agree fairly closely with those obtained from



TABLE III  
MODIFIERS WITH TRACER GROUPS IN STYRENE POLYMERIZATIONS

Type of polymerization	Modifier	Modifier (%)	Time (hours)	Temp. (°C)	Sulfur (%)	Mol. wt. (sulfur analysis)	Neut. or sapon. equiv.	Mol. wt. by osmotic pressure*	Mol. wt. by viscosity
Emulsion	Thioglycolic acid	4.8	18	50	0.25 0.13 0.22	12,800 24,600 14,600 (Av. 17,300)	19,900 20,200	17,000	6,000-8,000
Bulk	Thioglycolic acid	9.1	40	80	0.12	26,700	28,200	22,000	9,000-11,000
Emulsion	Ethyl thioglycolate	21.6	21.5	50	0.15 0.22	21,300 14,600 (Av. 18,000)	28,800 18,600 22,600		8,000-10,000
Emulsion	Ethyl thioglycolate	16.7	9	50	0.18 0.12	18,000 26,700 (Ab. 22,350)	22,900 23,600		11,000-16,000
Emulsion Bulk	Ethyl thioglycolate Thioglycolic acid	13.0 10.0	6	50 80	0.12 0.4-0.8	26,700 4,000-8,000	26,700 8,500-9,000		13,000-15,000

\* The authors are indebted to F. W. Banes for these measurements.

sulfur analysis and neutral equivalents. Viscosity measurements were made on each sample and again proved to be unsatisfactory.

Sulfur analyses were carried out by oxidation of the polystyrenes in a Parr bomb and determination of the sulfur gravimetrically as barium sulfate.

*10. Isolation of the Addition Product, *n*-Dodecyl  $\beta$ -Phenylethyl Sulfide, from Polymerization Reactions.*—Both emulsion and bulk polymerizations of styrene in which over 30 per cent by weight of *n*-dodecanethiol was present yielded mainly a high-boiling oil. This oil was taken up in ether and washed with 10 per cent sodium hydroxide solution, then with water, and dried over sodium carbonate. After removal of the ether, a portion of the oil was fractionally distilled. Most of it distilled as a clear, colorless liquid, boiling at 221–223° under 12 mm. pressure.

To a solution of 5 g. of the crude dried oil in an acetone–acetic acid mixture was added 5 cc. of 30 per cent hydrogen peroxide. The mixture was allowed to stand for two hours at room temperature with occasional shaking, and the mush of crystals which had formed was then filtered and dried. Three recrystallizations from 50 per cent ethanol gave lustrous crystalline leaflets, melting at 73–74°. Mixtures of these crystals with authentic *n*-dodecyl phenylethyl sulfoxide melted at 73–74°.

*Anal.* Calcd. for  $C_{20}H_{34}OS$ : C, 74.46; H, 10.63; S, 9.95. Found: C, 74.19; H, 10.45; S, 10.64.

*11. Preparation of Reagents. a. Thioglycolic Acid, its Sodium Salt and Esters.*—Thiodiglycolic acid was prepared according to the method of Friedländer and Chevala<sup>11</sup>. The disulfide was not isolated, but was reduced directly to thioglycolic acid, which was redistilled under reduced pressure in an atmosphere of nitrogen (b. p. 86–87° at 3 mm.). The sodium salt was prepared by neutralizing the acid with the calculated amount of sodium carbonate, precipitating the salt by the addition of alcohol, and drying with ether.

The ethyl ester was prepared by the ordinary esterification with absolute alcohol and a trace of sulfuric acid. The octyl ester was prepared by refluxing the acid and *n*-octyl alcohol in dry benzene with a small amount of *p*-toluenesulfonic acid. Water was extracted from the mixture as it was formed. The ester was washed with sodium carbonate, and distilled twice under reduced pressure in an atmosphere of nitrogen. The boiling point was 124° at 4 mm. pressure.

*b. 11-Mercaptoundecanoic Acid.*—A solution of 10-undecanoic acid in toluene to which a small amount of benzoyl peroxide had been added was treated with hydrogen bromide at 0° until saturated. The 11-bromoundecanoic acid crystallized when the solution was cooled to –10°, and it was recrystallized from chloroform. The pure bromo acid (m. p. 50–51°) was converted to the mercapto compound by refluxing with thiourea in alcoholic sodium hydroxide. Acidification of the solution yielded nearly pure 11-mercaptoundecanoic acid. After several recrystallizations from alcohol and ligroin, the melting point was 45°. Cohen<sup>12</sup> reports 47°.

*c. *n*-Dodecyl  $\beta$ -Phenylethyl Sulfoxide,  $C_{12}H_{25}SOCH_2CH_2C_6H_5$ .*—A solution of 5.1 g. (0.025 mole) of *n*-dodecanethiol and 1.44 g. (0.025 mole) of potassium hydroxide in 40 cc. of hot ethanol was prepared, and 4.62 g. (0.025 mole) of  $\beta$ -phenylethyl bromide was added dropwise to the stirred, hot solution. Potassium bromide precipitated during the course of the reaction. The mixture was refluxed for a half hour after addition of all the bromide; it was then diluted with water and the solution was extracted with ether. The ether solution was washed with 10 per cent sodium hydroxide solution, then with water, and dried over sodium carbonate.

The crude sulfide obtained by evaporating the ether was dissolved in 50 cc. of acetone and 10 cc. of glacial acetic acid. To this solution was added 6 cc. of 30 per cent hydrogen peroxide, and the oxidation was allowed to proceed at room temperature overnight. Lustrous, crystalline leaflets were obtained, which, after two recrystallizations from 50 per cent ethanol, melted at 73.5–74.0°.

**12. Polymerization of Styrene in the Presence of Diisopropylxanthic Disulfide.**—Bulk polymerizations with this modifier were effected in the same way as those with dodecanethiol, except that the reactions were carried out at the steam-bath and the time of polymerization was twenty-four hours. Emulsion polymerizations were effected in the same way as those with the thiol modifier, except that hydrogen peroxide was used as the catalyst. Details of the experiments are given in Tables IV and V.

TABLE IV  
BULK POLYMERIZATION OF STYRENE WITH DIISOPROPYLXANTHIC  
DISULFIDE AS MODIFIER

Trial	Styrene (g.)	Benzoyl peroxide (g.)	Modifier (g.)	Molecular weight*	Sulfur analyses (%)	Sulfur/ mole
1	4.9	0.05	0.05	7170	..	..
2	4.85	.05	.10	2650	..	..
3	4.75	.05	.20	2400	2.5	1.87
4	4.55	.05	.40	1110	..	..
5A	9.50	.10	.40	2305	1.17	0.84
5B				2570	1.17	0.94
6A	9.60	.20	.20	3000	1.82	1.70
6B				4650	1.82	2.64
7	9.60	.20	.20	3490	1.65	1.80
8	9.40	.20	.40	4640	2.50	3.6(?)
9	9.50	.10	.40	3100	..	..

\* Molecular weights were determined from viscometric measurements, using the Kemp-Peters equation<sup>4</sup>, with the exception of 5B and 6B, which were measured cryoscopically.

TABLE V  
EMULSION POLYMERIZATIONS OF STYRENE WITH DIISOPROPYLXANTHIC  
DISULFIDE AS MODIFIER\*

Trial	Styrene (g.)	H <sub>2</sub> O <sub>2</sub> (30%) (cc.)	Modifier (g.)	Molecular weight†	Sulfur analyses (%)	Sulfur/ mole
1	20.0	1.33	0.40	7400	2.49	5.75(?)
2	20.0	0.66	.20	6600	0.985	2.03
3	20.0	.66	.40	5000	1.20	1.88
4	20.0	.66	.80	3700	1.52	1.75
5	20.0	.66	1.60	2600	2.60	2.09
6	20.0	.66	3.20	‡	..	..

\* All polymerizations were run in 40 g. of 2.5% soap solution at 50° for twenty-four hours. † Molecular weights by cryoscopic method. ‡ No polymer was obtained.

## B. POLYBUTADIENE

**1. Polymerization of Butadiene in the Presence of *n*-Dodecanethiol.**—Polybutadiene was prepared only by the emulsion method, with 2.5 per cent aqueous solution of Ivory soap flakes as the stock emulsifier. The procedure for a typical run was as follows. Into a 4-ounce bottle was weighed 20 g. of the 2.5 per cent soap solution, and 0.10 g. of potassium persulfate, usually as a solution in 3 cc. of distilled water, was added. The bottle was chilled in an ice-salt

mixture and, when the contents had solidified, the *n*-dodecanethiol, varying in amount from 0.05 to 8 g., was added. Finally 10 g. of liquid butadiene was weighed in, and the bottle was sealed with a screw cap having a tinfoil gasket over a soft rubber base. The polymerization was effected by tumbling the bottle in a constant temperature water-bath at 50° for about twenty hours. The latex was then removed from the bottle and vented of excess butadiene, 0.1 g. of hydroquinone was added, and the polymer was coagulated with a dilute sodium chloride-sulfuric acid solution.

The sticky gums obtained from the polymerization reactions were washed well by treating them with steam. Most of the water was removed by washing with methanol. After one reprecipitation from benzene solution by the addition of methanol, the polymers were extracted in a Soxhlet thimble for eighteen hours with toluene-ethanol azeotrope. The resulting gums were dried, first in an oven at 75°, and then in a vacuum drying pistol.

**2. Determination of Molecular Weights.**—The low molecular weight polybutadienes were sticky gums and were very difficult to handle. Results obtained in molecular weight determinations were rather unsatisfactory. Cryoscopic measurement was the only method available since no constant had been determined for polybutadiene for use in the Kemp-Peters equation<sup>6</sup>. Benzene was used as the cryoscopic solvent. Results of these determinations are given in Table VI.

TABLE VI  
EMULSION POLYMERIZATIONS OF BUTADIENE WITH DODECANETHIOL  
AS MODIFIER

Run	Buta- diene (g.)	2.5% soap solu- tion (g.)	Dodec- anethiol (g.)	Dodec- anethiol (%)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g.)	Time (hours)	Temp. (° C)	Con- version (%*)	Sulfur analyses (%†)	Molecular weight cryoscopic	S/mole
1	10	20	0.00	0.00	0.1	20	50	30			
2	20	35	0.10	0.5	.09	12	50	46.5	0.18-0.19		
3	10	20	0.51	5.1	.25	20	50	70			
4	10	20	1.25	10.87	.25	20	50	50			
5	10	20	1.62	13.6	.35	16	50	0			
6	10	20	0.75	6.8	.35	16	50	80	0.9-1.01	2300	0.72
7	10	20	0.75	6.8	.35	18	50	80	.97-1.13	2100	.72
8	10	20	1.00	8.8	.35	18	50	74.0	0.95	2200	.65
9	10	20	0.75	6.8	.35	16	50	50	0.68	2500-2900	.5-0.6
10	10	20	.25	2.2	.10	20	50	90	0.75	2000	.47
11	10	20	.40	3.9	.10	20	50	90	0.68		
12	10	20	.085	0.84	.00	20	50	0.00			
13	20	40	2.0	9.8	.50	20	50	..	1.4-1.8		
14	10	20	6.8	41.0	.50	16	50	..	10.03		
15	10	20	8.5	46	.10	20	50	..			

\* Based on weight of polymer obtained. † The authors are indebted to G. D. Sands for these analyses.

**3. Sulfur Analyses.**—Since the low molecular weight polybutadienes were gums, they could not be obtained in the finely divided form essential for oxidation by the Parr bomb method. A wet oxidation method was used, following essentially the procedure described by Cheyney<sup>13</sup>.

About 0.5 g. of polymer was weighed accurately into a 500-cc. Erlenmeyer flask. A fresh zinc oxide-nitric acid mixture was prepared by adding 10 g. of zinc oxide to 50 cc. of concentrated nitric acid, and 15 cc. of this solution was added to the sample in the flask. The flask was covered with a watch glass and allowed to stand for several hours at room temperature to ensure thorough wetting of the sample. About 15 cc. of technical fuming nitric acid was then added and the flask was whirled to prevent ignition of the polymer during oxidation. When solution was complete, 5 cc. of saturated aqueous

bromine was added, and the solution was slowly evaporated on a hot plate. During the evaporation, small amounts of potassium chlorate were added to the boiling mixture. Evaporation was carried to dryness, and the residual salts were baked until all the nitrates were decomposed, as indicated by the absence of brown fumes. The residue was dissolved in dilute hydrochloric acid, and the solution was analyzed for sulfur, either by gravimetric determination as barium sulfate, or by the volumetric procedure of Luke described in the experimental section of the following report on the sulfur analysis of GR-S.

Comparison of the sulfur analysis with the cryoscopic molecular weight gives the ratio of sulfur atoms per polymer molecule.

The results of these determinations are given in Table VI.

4. *Addition Compounds of Butadiene and n-Dodecanethiol.*—When *n*-dodecanethiol was employed in amounts of 40 per cent or more of that of the butadiene in polymerization reactions, the product was a heavy oil. The oil from one polymerization mixture, which had been charged with 10 g. butadiene, 8.5 g. of *n*-dodecanethiol, and 0.1 g. of potassium persulfate, was washed well with methanol and then taken up in ether and dried over magnesium sulfate. After removal of the ether, the oil was distilled in an all-glass apparatus incorporating a small modified Claisen flask. No sharp fractionation could be effected with this apparatus, and the boiling point rose steadily from 120 to 220°, where distillation was stopped. That this boiling range is indicative of a mixture was supported by cryoscopic molecular weight determinations made on two arbitrary fractions. A fraction boiling at 120–150° at 5 mm. pressure had an average molecular weight of 238; while a second fraction, boiling at 155–200° at 5 mm. pressure, had an average molecular weight of 307. These values correspond roughly to molecular weights of addition products from one mole of dodecanethiol and one and two moles, respectively, of butadiene.

The higher boiling fraction contained 9.62 per cent sulfur. This compares favorably with the theoretical value of 10.34 per cent sulfur present in the addition product of two moles of butadiene and one mole of dodecanethiol.

5. *Cleavage of Butadiene-dodecanethiol Addition Product to 1-Dodecanesulfonyl Chloride.*—The oil from a polymerization reaction which had been charged with 10 g. of butadiene and 6.8 g. of *n*-dodecanethiol was washed well with methanol, taken up in ether and dried over magnesium sulfate. After removal of the ether, the oil was distilled at 5 mm. pressure. The boiling point rose fairly steadily from 120 to 180°, where the distillation was stopped. A fraction of 1 cc. was taken at 160–161°, and a sulfur analysis was made on this liquid. It contained 10.03 per cent of sulfur, which compares favorably with a theoretical value of 10.34 per cent for a structure containing two moles of butadiene and one of dodecanethiol.

About 0.7 g. of this liquid fraction, boiling at 160–161° at 5 mm. pressure, was dissolved in 10 cc. of glacial acetic acid. A little water was added, and chlorine gas was bubbled slowly through the solution. This follows the method of Lee and Dougherty<sup>6</sup> for the oxidative cleavage of organic sulfides. The reaction mixture was kept at about room temperature by cooling the flask externally with cold water. When the solution had become saturated with chlorine, it was poured into a beaker filled with crushed ice. An oily precipitate was collected, dried, and recrystallized several times from methanol. The resulting crystals melted at 42–43°. Sprague and Johnson<sup>14</sup> report the melting point of 1-dodecanesulfonyl chloride as 42.5°.

To a solution of 0.2 g. of the sulfonyl chloride in 10 cc. of ethanol was added 5 cc. of concentrated aqueous ammonia, and the mixture was placed on a



mechanical shaker for two hours. It was then refluxed for fifteen minutes, and finally poured into 25 cc. of ice water. The white solid precipitate was dissolved in 10 per cent sodium hydroxide solution. This solution was filtered and then acidified to reprecipitate the sulfonamide. One recrystallization from methanol gave a compound melting at 93–94°. Sprague and Johnson<sup>14</sup> report the melting point of dodecanesulfonamide as 95.4°.

6. *Ozonization of a Butadiene-Dodecanethiol Addition Compound.*—A sample of the oil having a molecular weight of 307 and a sulfur content of 9.62 per cent, and believed to be mainly a mixture of the isomers resulting from the addition of one mole of *n*-dodecanethiol to two moles of butadiene, was examined.

A solution of 4.15 g. of the oil in 100 cc. of chloroform was ozonized<sup>15</sup>. After removal of the chloroform, the ozonide was cleaved with 100 cc. of 5 per cent hydrogen peroxide. The aqueous solution of the cleavage product was distilled to a residual volume of about 5 cc. The distillate was diluted to 250 cc.

Aliquot portions of the distillate were analyzed for total formic acid by a modification of the method of Reid and Weihe<sup>16</sup>. In this method of analysis the formic acid is oxidized to carbon dioxide by means of an acetic acid solution of mercuric acetate. The carbon dioxide is determined by absorption by Ascarite. The amounts from two portions corresponded to 0.0059 and 0.0060 mole of carbon dioxide from the original sample of oil ozonized. This indicates that about 22.4 per cent of the butadiene units in the addition product are present as 1,3-butadiene residues arising from 1,2-addition. With other samples of the oil, values as high as 32 per cent were found. The range is almost the same as that (23–36 per cent) found by the application of the same ozonolysis and analytical techniques to GR-S<sup>17</sup>.

#### C. HYDROGENOLYSIS OF A BUTADIENE-STYRENE COPOLYMER

A copolymer was prepared from 40 g. of a mixture of butadiene and styrene (3–1 by weight) in the presence of a g. of dodecanethiol; the emulsion polymerization technique described above in connection with polybutadiene was employed. The polymer was washed once with water and twice with methanol. To ensure complete removal of any unchanged thiol, the polymer was dissolved in benzene and precipitated by addition to a large excess of methanol, and it was finally extracted with acetone in a Soxhlet apparatus. The sulfur content of the dried material was 0.80–0.83, and the viscometric molecular weight was 4600.

A 20-g. sample of the purified polymer was dissolved in 300 cc. of cyclohexane and butanol (about 150 cc.) was added to the point of incipient precipitation. About 75 g. of Raney nickel was added, and the mixture was heated on a steam cone for twelve hours. The mixture was treated as described above in connection with the hydrogenolysis of polystyrene, yielding about 1 g. of an oil which on redistillation gave 0.5 g. of pure dodecane, b. p. 114–115° (34 mm.) (lit.<sup>8</sup>, 114° (30 mm.)),  $n_D^{20}$  1.4188 (lit.<sup>9</sup> 1.41967).

Anal. Calcd. for  $C_{12}H_{26}$ : C, 84.61; H, 15.39. Found: C, 84.70; H, 15.50.

#### DISCUSSION

The molecular weight of polystyrene formed by either bulk or emulsion polymerization in the presence of *n*-dodecanethiol is inversely proportional to the thiol concentration, and the polymers contain approximately one atom of sulfur per molecule (Sections A-1 to A-4, Tables I and II). Although the at-



tempted cleavage of the thiol residue from a modified polymer by the action of chlorine was not successful (Section A-5), the isolation of dodecane by hydrogenolysis over Raney nickel catalyst (Section A-6) and the agreement of sulfur content with carboxyl or carbalkoxyl content in polymers prepared in the presence of carboxy- or carbalkoxy thiols (Sections A-7 to A-9, Table III) show that thiol modifiers are incorporated into the polymers. The less extensive studies with diisopropylxanthic disulfide as a modifier (Section A-12) show that the inverse relationship between modifier concentration and molecular weight also obtains with this modifier.

Polybutadienes of low molecular weight, prepared in the presence of dodecanethiol, were less satisfactory materials for study than similar polystyrenes. However, the progressive change in physical state, from rubberlike materials through sticky semisolids to viscous oils, with increasing modifier concentration indicates a decrease in molecular weight with increase of modifier. In view of the experimental difficulties in the determination of the molecular weights and sulfur contents of these polymers, the agreement between the observed value of about 0.6 sulfur atom per molecule and the theoretical value of 1.0 is reasonably good (Sections B-1 to B-3, Table VI). The isolation of pure dodecane from the products of hydrogenolysis of a butadiene-styrene copolymer (Section C) shows that the thiol modifier enters the copolymer molecule. The fraction composed of one molecule of dodecanethiol and two molecules of butadiene (Section B-4 to B-6) is of especial interest because it represents the simplest possible modified polybutadiene, and any effect which the modifier might have in directing the mode of reaction of butadiene (as, for example, by repressing 1,2-addition) should be easily detected. Attempts to separate pure compounds from this fraction were unsuccessful, and attempts to prepare sulfoxides, which might have been separable, gave explosive peroxides. However, the ozonolysis of the fraction (Section B-6) shows that the relative content of 1,4- and 1,2-butadiene residues is essentially the same as that of GR-S prepared in the presence of very much less modifier; thus it appears unlikely that the modifier has any effect on the mode of reaction of butadiene.

All the observations made in this study are in agreement with the predictions of the chain-transfer theory of modifier action.

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## THE MECHANISM OF MODIFIER ACTION IN GR-S POLYMERIZATION. II \*

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The preceding paper<sup>1</sup> discusses the theory of modifier action in GR-S polymerization. Briefly the theory assumes that certain compounds, such as thiols, can act as transfer agents<sup>2</sup> for growing free radical chains. The net effect of this action is to reduce the molecular weight of the polymer and to keep it more soluble. Assuming that chain transfer occurs much more frequently than initiation and termination, it follows that practically every polymer molecule will have incorporated in it one modifier fragment. Experimental support for the theory was obtained by studies on various polymer systems<sup>1</sup>, which, however, did not include direct measurements on commercial GR-S.

To provide further evidence for the chain transfer-free radical mechanism of polymerization<sup>2</sup>, a number of careful molecular weight measurements and sulfur determinations were carried out on certain portions of GR-S samples. The purpose of these measurements was to find the average number of sulfur atoms per molecule of polymer. If the number found was close to unity, then that would provide further support for the above-mentioned theory.

Several difficulties were encountered in the determination of molecular weights and sulfur contents of GR-S. In the first place, GR-S is highly heterogeneous, so it was found desirable to fractionate the material before making the measurements. Secondly, the very low sulfur content in the fractions of interest necessitated the development of special techniques for the quantitative determination of those small amounts of sulfur. Finally, the molecular weights had to be determined osmotically, since only number average molecular weights would serve the purpose in mind.

Since an appreciable fraction of each of the GR-S samples investigated was insoluble in benzene and similar solvents, the gel fraction had to be removed if meaningful molecular weights were to be obtained. In addition the very low molecular weight material present in GR-S also had to be removed to make possible significant osmotic pressure measurements on the bulk of polymer. If the low molecular weight material were not removed, the membranes used would have to be so impermeable that osmotic equilibrium could not be attained in a reasonable length of time. Accordingly, the fraction investigated was taken as that portion which was soluble in benzene but insoluble in a mixture consisting of equal volumes of benzene and methanol.

### EXPERIMENTAL PROCEDURE

Considerable care had to be exercised in preparing the polymer for osmotic measurements. In particular the effects of heat, light, and long drying had to

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be avoided. The best results were obtained when the following procedure was adopted.

About 10 g. of GR-S was extracted in the dark at room temperature by cycling acetone through the sample. The extracted sample was dried for nine hours in a vacuum desiccator and then placed in a large Erlenmeyer flask and covered with two liters of c.p. benzene. The polymer was permitted to dissolve by allowing the system to stand for three and one-half days at room temperature. The gel was removed by filtering through an 80-mesh Monel metal screen covered with glass wool.

After removal of the gel, the polymer was subjected to partial fractional precipitation by adding the solution to an equal volume of methyl alcohol. The resulting polymer suspension was then coagulated with a small amount of sodium chloride. Following coagulation the sample was washed with water and with alcohol, after which it was dried in a vacuum desiccator for nineteen hours. About 1 g. of this material was dissolved in 200 cc. of c.p. distilled benzene, and portions of this solution were diluted for osmotic pressure measurements.

The osmotic pressures were measured by means of glass osmometers<sup>3</sup> immersed in a thermostatically controlled water-bath. The membranes employed were made of no. 300 non-moistureproof cellophane, which was treated with 60 per cent zinc chloride solution according to the method of McBain and Stevens<sup>4</sup> for the purpose of swelling the material to the proper permeability. The nature of the membrane depended a great deal on the concentration of the solution in which it was swollen, and many of the membranes had to be discarded because of the improper permeability characteristics. The membranes were sealed to the osmometers by means of polyvinyl alcohol and were kept soft during storage by having them immersed in benzene containing a trace of triethylene glycol and water.

The height of the column of solution above that of the solvent was measured by means of a cathetometer. To make sure that osmotic pressures were really being measured, the level of the solution in the capillary tube was initially set at a point below the equilibrium level, adjustments being made if necessary after observing the early effects. (The system was, of course, allowed to reach temperature equilibrium before any osmotic tendencies were observed.) The level of the solution was then observed as a function of time by means of periodic cathetometer readings. The level would always reach a maximum in the course of several hours, after which it would fall off slowly as a result of diffusion of solute through the membrane. The time required to reach the maximum depended on the initial difference in heights and on the porosity of the membrane. When approximate information was available on certain samples, the measurements could be expedited by starting the system near equilibrium. If the falling off of height after the maximum was reached proved to be very rapid, the measurement was discarded. When the rate of diffusion of solute through the membrane was slow, a correction for that diffusion could be applied by extrapolating to zero time, but usually that correction was small enough to be neglected.

Measurements were made at several different concentrations for each solution investigated. The equilibrium solution rise was corrected for the capillary rise of the solvent in each case. In analyzing the results, the best quadratic function of the form:

$$h = ac + bc^2 \quad (1)$$

was determined for each sample by the method of least squares. In Equation (1),  $h$  represents the corrected osmotic rise in centimeters and  $c$  the concentration in grams per 100 cc. of solution. With benzene as a solvent at 30.4° (the temperature of the experiments), the molecular weight can be calculated by means of the equation:

$$M = \frac{2.96 \times 10^5}{(h/c)_0} \quad (2)$$

where

$$(h/c)_0 = \lim_{c \rightarrow 0} h/c = a \quad (3)$$

Sulfur was determined in the prepared samples of GR-S by a combination of the methods of Luke<sup>5</sup> and of Cheyney<sup>6</sup>. The procedure involved the complete oxidation of the sample by means of fuming nitric acid, bromine, and potassium chlorate. Excess oxidizing agents were removed by prolonged heating of the solid materials, followed by successive additions of hydrochloric acid and further evaporations to dryness.

The sulfate resulting from the oxidation was reduced by adding some hydrogen iodide reagent, and the hydrogen sulfide generated was distilled into a cadmium chloride solution. An excess of standard 0.01 *N* potassium iodate solution was added to the latter solution, which was then back-titrated with standard 0.01 *N* sodium thiosulfate solution, using starch as indicator.

Because of the small amounts of sulfur involved, blank determinations had to be carried out to correct for the sulfur present in the reagents used. Using the best grade of reagents available, blanks amounted to as much as 0.006 milliequivalent of sulfur, which in extreme cases was equivalent to 40 per cent of the total sulfur found by the final titration. This source of error is the most serious in the whole procedure and is the principal cause of uncertainty in the results.

#### EXPERIMENTAL RESULTS

A summary of osmotic results, molecular weights, sulfur contents and atoms of sulfur per molecule is given in Table I. The values of  $(h/c)_0$  were computed by the method of least squares from at least eleven and sometimes

TABLE I

Polymer	$(h/c)_0$	Molecular weight	Sulfur (%)	Atoms of sulfur per molecule
A <sub>1</sub>	8.870	33,300	0.071	0.3
A <sub>2</sub>	9.100	32,600		
B <sub>1</sub>	8.510	34,800	0.064	0.69
B <sub>2</sub>	8.540	34,600		
C	5.959	49,740	0.0728	1.13

as many as sixteen osmotic pressure measurements. Of the results given in Table I, the values for Polymer C are the most accurate, since the greatest precautions were taken in preparing that sample and in carrying out the sulfur analyses.

#### DISCUSSION

In discussing these results, it should be made clear that the commercial GR-S samples used were among the first ones made in the government program, and accordingly must not be regarded as representing the current product.

The particular samples investigated had considerable gel, so the average molecular weight of the soluble portion was low. This was true because gelation preferentially removes large molecules. However, this should not seriously alter the theoretical interpretation to be attached to the results.

It should be recognized that several effects can arise which bring about deviations from the one-to-one correspondence between sulfur atoms and polymer molecules. First of all, it is possible that radical chains can be terminated by disproportionation or combination, which would have the effect of modification without thiol consumption. This process would tend to lower the sulfur content per molecule. Secondly, cross-linking reactions doubtless take place, which tend to increase the number of sulfur atoms per molecule. If cross-linking goes far enough, the molecules so affected become incorporated into a gel structure which is insoluble. Since the experiments were carried out only on the soluble portion, it is clear that gelation should not affect the interpretation advanced. Only the moderate, cross-linked molecules which remain soluble affect the sulfur-polymer ratio.

The amount of sulfur in the fractions of interest was found to be in the neighborhood of 0.07 per cent with a probable error amounting to about 5 or even 10 per cent of that figure. The precautions which had to be taken for the accurate determination of such small amounts of sulfur were discussed in the experimental section. The osmotic molecular weights varied from 33,000 to 50,000 for the different samples with probable errors equal to about 5 per cent.

From some of the earlier determinations it was calculated that an average of about 0.7 atom of sulfur was present per molecule. The way the early experiments were carried out suggested that the figure 0.7 was experimentally too low, so more accurate experiments were conducted on a small number of samples. The best experiments indicated 1.1 atoms of sulfur per molecule. Although the figures 0.7 and 1.1 have large probable errors, they are sufficiently close to unity to lend support to the free radical-chain transfer mechanism. Considering the difficulties involved, the figure 1.1 in particular (which was the result of the most accurate measurements) must be regarded as being compatible with theory.

### SUMMARY

The chain transfer theory of modifier action has been tested on commercial GR-S by means of molecular weight and sulfur content determination. The number of sulfur atoms per molecule was found to range between 0.7 and 1.1, to be compared to the theoretical value of unity. In view of the experimental difficulties involved, the results are considered to be in good agreement with the theory.

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## DETERMINATION OF HYDROPEROXIDES IN RUBBER AND SYNTHETIC POLYMERS \*

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Ferrous iron has been used as a reagent for the determination of peroxide by numerous investigators. Yule and Wilson<sup>1</sup> estimated peroxide in cracked gasoline by shaking with an acid solution of ferrous thiocyanate and back-titrating the resulting ferric salt with titanous chloride. The method was criticized by Young, Vogt, and Nieuwland<sup>2</sup>, who used the color of the resulting ferric thiocyanate complex as a basis for a colorimetric determination of peroxide. In this procedure methanol was used as the solvent. Bolland, Sundralingam, Sutton and Tristram<sup>3</sup> modified the method to enable rubber samples to be analyzed by changing the solvent to a mixture of benzene and methanol (73 per cent benzene by volume).

For determining peroxide in GR-S (butadiene-styrene copolymer) and other butadiene copolymers it would be desirable to employ a solvent rich in benzene, since these polymers tend towards insolubility upon oxidation. A solvent composed largely of benzene would also improve the sensitivity of the determination, since larger quantities of polymer could be dissolved in a given volume of solvent.

There are several disadvantages inherent in the use of thiocyanate as a color reagent for iron<sup>4</sup>. The intensity of the color depends on the concentration of thiocyanate and on the acid concentration, and varies with the presence of various ions which form complexes with iron. In practice, a large excess of thiocyanate is used to lower the effects of acid and interfering ions and to give a closer approximation to Beer's law. The red color of the ferric thiocyanate complex is somewhat unstable, requiring colorimeter readings to be made without undue delay. The ferrous thiocyanate reagent of Bolland, Sundralingam, Sutton and Tristram<sup>4</sup> and Robey and Wiese<sup>5</sup> is so unstable that it must be freshly prepared every few hours and stored in the dark.

The advantages of *o*-phenanthroline as a color reagent for iron have been recognized by many investigators<sup>6</sup>. Its complex with ferrous iron is very stable, its solutions showing no change in color for many months. Beer's law is closely obeyed. The intensity is not so strongly affected by the concentration of excess reagent or of acid, as in the case of the thiocyanate complex. Since large concentrations of inorganic salts are not needed, it should be possible to use a solvent consisting largely of benzene, with only a small amount of methanol. Solutions of ferrous salts in methanol under nitrogen and *o*-phenanthroline in benzene are stable and can be stored indefinitely without noticeable change.

The effects of complexing agents on the oxidation potential of the ferrous-ferric ion system are of interest. Thiocyanate lowers the oxidation potential, making the oxidation of the ferrous ion proceed more readily. This shift is

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advantageous in making the reagent very reactive toward polymer peroxides but also accounts for its extreme sensitivity to air oxidation. *o*-Phenanthroline has just the opposite effect<sup>7</sup>; the ferrous *o*-phenanthroline complex is not appreciably oxidized by polymer peroxides, and it is entirely stable with respect to air oxidation. To increase the reactivity with polymer peroxides, uncomplexed ferrous iron was first tried as a reagent. As will be seen below, satisfactory results were obtained under the proper conditions, provided that no antioxidant was present in the polymer. In the presence of antioxidant, incomplete reduction of rubber peroxide was observed. It was found that the addition of phosphoric acid (which lowers the ferrous-ferric oxidation potential) made the reaction proceed satisfactorily even in the presence of antioxidant. Nitric acid was added to prevent a color due to solvolysis of ferric iron.

Farmer and Sutton<sup>8</sup> observed that natural rubber forms only peroxides of the hydroperoxide type. In the present investigation, numerous synthetic polymers, including polyisoprene, polybutadiene, and copolymers of isoprene or butadiene with styrene, acrylonitrile, and other vinyl-type monomers, were found to form peroxides which reacted at the same rate as natural rubber peroxides with the test reagent. Since disubstituted organic peroxides failed to react<sup>8</sup>, this observation is evidence that all the polymers studied form peroxides of the hydroperoxide type.

#### PROCEDURE

This method is intended for the determination of relative amounts of hydroperoxides in natural rubber, and various synthetic polymers and copolymers. It is applicable only to hydroperoxides, and except for this limitation it can be used generally for compounds of low molecular weight as well as high polymers.

#### PREPARATION OF SOLUTIONS

**Ferrous Iron Solution.**—Remove the dissolved oxygen from 1 liter of methanol by bubbling nitrogen through it for 30 minutes. Dissolve 19.605 grams of ferrous ammonium sulfate hexahydrate,  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , in the methanol containing 13.9 cc. of concentrated sulfuric acid to make the solution about 0.25 *M* in sulfuric acid. If stored under an atmosphere of nitrogen, this solution is stable for a long time. For use over a period of a few days, 10-cc. portions can be allowed to stand in air.

Each day a 0.002 *N* working solution is prepared by diluting 2 cc. of the 0.05 *N* solution to 50 cc. with methanol but without adding acid.

**Nitric Acid-Methanol Solution.**—Add 1 cc. of concentrated nitric acid to 20 cc. of methanol slowly and with cooling. One milliliter of this solution provides 0.05 cc. of concentrated nitric acid.

**Phosphoric Acid-Methanol Solution.**—Prepare a 1 *M* stock solution by adding 6.75 cc. of 85 per cent phosphoric acid (14.8 *M*) to sufficient methanol to prepare 100 cc. of solution. Dilute the 1 *M* solution to 0.04 *M* for use as a working solution; 0.5 cc. of 0.04 *M* solution provides 0.02 millimole of phosphoric acid.

***o*-Phenanthroline Solution.**—Dissolve 1 gram of *o*-phenanthroline monohydrate in 1000 cc. of thiophene-free benzene.

#### ANALYSIS OF UNKNOWN SAMPLES

Pipet 1 cc. of rubber solution (containing about 1 gram of polymer per 100 cc. of benzene) into a 50-cc. volumetric flask. Add about 25 cc. of thiophene-

free benzene, washing any polymer solution from the sides of the flask. Add 1 cc. of nitric acid-methanol solution and 0.5 cc. of 0.04 *M* phosphoric acid (methanol), shaking well after each addition. Pipet 1 cc. of 0.002 *M* ferrous iron into the flask, shake well, and allow the mixture to stand at least 15 minutes. Add 3 to 5 cc. of *o*-phenanthroline solution and make up to 50 cc. with thiophene-free benzene. Read the transmission value at 508  $m\mu$  with a spectrophotometer or use a photoelectric colorimeter provided with a filter showing maximum transmission at 500 or 510  $m\mu$  (preferably not 520  $m\mu$ ), comparing the transmission with that of benzene.

If the transmission value lies between 50 and 70 per cent, calculate the active oxygen content as shown below. Otherwise, estimate the adjustment necessary in sample size required, and repeat the determination. For samples of entirely unknown peroxide content, it is advisable to vary the sample size, using 0.1, 1, and 10 cc. of polymer solution in the preliminary estimation. If a 10-cc. sample is used, or if the sample is highly colored, a diluted benzene solution of polymer should be used instead of benzene for the comparison liquid in the optical measurement.

#### CONSTRUCTION OF CALIBRATION CURVE

Using a graduated 1-cc. pipet, add the following amounts of 0.002 *N* ferrous iron solution to a series of 50-cc. volumetric flasks: 0.2, 0.4, 0.6, 0.8, and 1.0 cc. Add about 25 cc. of benzene to each flask, washing the walls carefully. Complex the ferrous iron with 3 to 5 cc. of *o*-phenanthroline solution and make up to 50 cc. with benzene. Take colorimeter or spectrophotometer readings relative to benzene.

Compute the optical density of each solution from the equation  $D = \log I_0/I$ , and construct a graph of optical density against concentration of iron (expressed as equivalents of ferrous iron per 50 cc.). A straight line, corresponding to Beer's law, should be obtained.

#### CALCULATIONS

From the calibration curve the amount of iron remaining unoxidized can be read directly. By difference the amount of iron oxidized is determined. Each equivalent of iron oxidized corresponds to one equivalent or 8 grams of active oxygen. The active oxygen content is calculated as parts per million parts of solid polymer. If a polymer is only partly soluble, the concentration of the soluble polymer is determined by evaporation of an aliquot portion of the solution, and the calculation is based on the soluble part only.

$$\frac{(A - B) \times 8 \times 10^6}{C \times V} = \text{micrograms of active oxygen per gram of polymer} \\ = \text{p.p.m. active oxygen}$$

where *A* = equivalents of ferrous iron taken

*B* = equivalents of ferrous iron remaining

*C* = concentration of polymer grams per cc. of benzene

*V* = cc. of polymer solution used

#### DEVELOPMENT OF METHOD

*Spectrophotometric Curves of Standard Iron Solutions.*—A 0.05 *N* stock solution of ferrous iron was prepared by dissolving ferrous ammonium sulfate,  $\text{FeSO}_4(\text{NH}_4)\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , in air-free methanol, with sufficient concentrated sul-

furic acid added to make the solution 0.25 *M* in acid. The solution was stored under nitrogen and by occasional titration with ceric sulfate was found to be stable indefinitely. A 0.002 *N* working solution was freshly prepared each day by diluting 2 cc. of the stock solution to 50 cc. with methanol.

A 0.1 per cent solution of *o*-phenanthroline in benzene was used as the indicator solution. Various amounts of iron from  $2.5 \times 10^{-4}$  to  $2.5 \times 10^{-3}$  milliequivalent were treated with 6 cc. of indicator solution, and diluted to 25 cc. with benzene, and the absorption curves were determined with a Cenco-Sheard spectrophotometer. In agreement with Fortune and Mellon<sup>9</sup> for aqueous solutions, the maximum absorption was found at 508  $m\mu$ .

Calculation of the optical density at the wave length of maximum absorption and plotting against concentration showed that Beer's law was being closely followed over the concentration range studied.

*Effect of Acids on Ferrous and Ferric Complexes.*—Preliminary experiments showed that, while the concentration of excess indicator could be varied over wide limits without affecting the absorption at 508  $m\mu$ , the acidity of the solution is of considerable importance. If the acidity is too low, the ferric ion shows appreciable absorption, apparently because of partial solvolysis of the *o*-phenanthroline complex. By complete oxidation of a solution of ferrous iron, the usual yellow color of ferric iron appeared. When *o*-phenanthroline was added, a deeper yellow color appeared instead of the usual blue color obtained in aqueous solutions. With a larger excess of acid, absorption at 508  $m\mu$  by the ferric complex could be eliminated, but the ferrous *o*-phenanthroline complex then became unstable.

A series of experiments was performed in which conditions were sought that would give the maximum transmission for ferric iron and the minimum for ferrous iron at 508  $m\mu$ . In each experiment a known amount of standard ferrous ammonium sulfate in methanol or standard ferric chloride, prepared by dissolving sublimed ferric chloride in methanol, was used. The iron solution, in a 50-cc. volumetric flask, was treated with 25 cc. of benzene. Five milliliters of 0.1 per cent benzene solution of *o*-phenanthroline was added. After addition of the acid being investigated and just sufficient methanol (1 to 2 cc.) to keep the acid in solution, the volume was made up to 50 cc. with benzene. The spectrophotometric transmission value was determined at 508  $m\mu$  at different time intervals after complexing, using benzene as a comparison liquid.

TABLE I  
EFFECT OF SULFURIC ACID ON FERRIC COMPLEX

0.002 <i>N</i> iron complexed (cc.)	Concentrated $H_2SO_4$ (cc.)	Time of standing		Transmission	
		$t_1$ (min.)	$t_2$ (min.)	$I_1$ (%)	$I_2$ (%)
1.0	0.00	95	1200	87	85
1.0	0.02	95	1200	98	97
1.0	0.05	95	1200	99.5	98.5
1.0	0.08	95	1200	99.5	99
1.0	0.0	90	360	81	78
1.0	0.1	90	360	100	99
1.0	0.2	90	360	100	100
1.0	0.4	90	360	100	100
3.0	0.0	90	1200	80	80
3.0	0.1	90	1200	99	78
3.0	0.2	90	1200	98.5	98
3.0	0.4	90	1200	99	99

TABLE II  
EFFECT OF SULFURIC ACID ON FERROUS COMPLEX

0.002 N iron complexed (cc.)	Concentrated H <sub>2</sub> SO <sub>4</sub> (cc.)	Time of standing (min.)	Transmission (%)
1.0	0.00	45	34
1.0	0.02	45	62
1.0	0.05	45	68.5
1.0	0.08	45	69
1.0	0.0	45	34
1.0	0.1	45	62
1.0	0.2	45	65
1.0	0.4	45	69

The results for sulfuric acid are shown in Tables I and II and for nitric acid in Table III.

Similar data for trichloroacetic acid showed that the ferrous complex was unaffected but that the absorption by the ferric complex could not be removed. Hydrochloric acid prevented absorption by the ferric complex but decomposed the ferrous complex.

Nitric acid is the only acid tried that will remove the absorption by the ferric complex at 508 m $\mu$  and yet not affect the ferrous complex. Not more than 0.1 cc. of concentrated acid can be used per 50 cc. of solution. Using this amount of acid, the absorption by the ferrous complex is not affected, and only 5 per cent absorption is found for the ferric complex.

*Effect of Time, Temperature, and Acid on Reaction between Polymer Peroxide and Ferrous Iron.*—A polymer of relatively high peroxide content was desired.

A laboratory GR-S sample was heated in air at 70° for 2 hours. The polymer was allowed to stand with 100 cc. of benzene for each gram of polymer:

TABLE III  
EFFECT OF NITRIC ACID

0.002 N iron complexed (cc.)	Concentrated HNO <sub>3</sub> (cc.)	Time of standing		Transmission	
		t <sub>1</sub> (min.)	t <sub>2</sub> (min.)	I <sub>1</sub> (%)	I <sub>1</sub> (%)
		On Ferric Complex			
1.0	0.00	15	60	94	94
1.0	0.02	15	60	95	95
1.0	0.05	15	60	95	95
1.0	0.08	15	60	95	94.5
1.0	0	960	..	76.5	..
1.0	0.2	960	..	96	..
1.0	0.5	960	..	96	..
1.0	1.0	960	..	98	..
On Ferrous Complex					
1.0	0.00	15	60	34	34
1.0	0.02	15	60	34	34.5
1.0	0.05	15	60	34	34.5
1.0	0.08	15	60	34	34.5
1.0	0.0	960	..	34	..
1.0	0.1	960	..	36	..
1.0	0.3	960	..	83	..
1.0	0.5	960	..	95	..

the gel was filtered off with a 100-mesh stainless steel screen. The resulting solution contained 0.0088 gram of soluble polymer per cc. Preliminary experiments showed that 1 cc. of this polymer solution gave a convenient extinction value when allowed to react with 1 cc. of 0.002 *N* ferrous iron.

Experiments were run as described in the previous section, using 1 cc. of polymer solution, 1 cc. of 0.002 *N* ferrous iron, and 0.1 cc. of nitric acid, except as noted. The solutions containing ferrous iron, polymer, and acid were allowed to stand various lengths of time at room temperature before the *o*-phenanthroline was added. No oxidation of iron occurred in the presence of the indicator. In certain experiments the mixture was heated to boiling and kept at the boiling point for the desired time. In these instances the acid was not added until after cooling and complexing, as the acid would oxidize the ferrous iron in hot solutions.

The data in Table IV indicate that the reaction between polymer peroxide and ferrous iron is complete in 15 minutes at room temperature if acid is present. No increase in transmission was obtained by heating up to 60 minutes. The

TABLE IV  
EFFECT OF TIME, TEMPERATURE, AND ACID ON THE REACTION OF RUBBER  
PEROXIDES AND FERROUS IRON

Con- centrated HNO <sub>3</sub> (cc.)	Tempera- ture	Time of reaction (min.)	Time after complexing		Transmission	
			<i>t</i> <sub>1</sub> (min.)	<i>t</i> <sub>2</sub> (min.)	<i>I</i> <sub>1</sub> (%)	<i>I</i> <sub>2</sub> (%)
0.1	Cold	5	30	..	64	..
0.1	Cold	10	30	..	67.5	..
0.1	Cold	15	30	960	69	64
0.1	Cold	20	30	..	69.5	..
0.1	Cold	30	55	180	69.5	68
..	Cold	30	40	..	64	..
0.1	Hot	15	30	960	66	62
..	Hot	15	30	960	67	60
0.1	Hot	30	30	960	70	66
..	Hot	30	30	960	70	64
0.1	Hot	60	30	120	70	69.5

final solutions were stable with respect to transmission values for periods of 1 to 2 hours, with only slight effects over longer periods of time. In all cases a more stable color was obtained in the presence of acid.

*Effect of Concentration of Excess Ferrous Iron.*—To determine whether an excess of ferrous iron is necessary for complete reduction of the rubber peroxides, the same polymer solution and procedure were used as in the previous section, allowing reaction times of 15 and 30 minutes at room temperature. The results are given in Table V.

From Table V it appears that with an increasing excess of ferrous iron a higher apparent peroxide content is in general obtained. As is shown below, this trend is caused by a variable amount of air oxidation of the excess ferrous iron. By limiting the observed transmission range to 50 to 70 per cent, a maximum deviation of around  $\pm 20$  per cent in apparent peroxide content is allowed, according to Table V. Considering the difficulty of sampling solid polymers and the relative nature of the method, this variation is not serious for following trends in polymer peroxides.

*Effect of Antioxidant.*—To determine the effect of antioxidant, 2 per cent of phenyl- $\beta$ -naphthylamine (based on the dry polymer) was added to the polymer solution already studied. With antioxidant present, hardly any oxidation of the ferrous iron occurred either at room temperature or upon heating.

TABLE V  
EFFECT OF CONCENTRATION OF EXCESS FERROUS IRON

Polymer solution (cc.)	0.002 N ferrous iron (cc.)	Time after complexing		Transmission		Active* oxygen (p.p.m.)
		$t_1$ (min.)	$t_2$ (min.)	$I_1$ (%)	$I_2$ (%)	
0.2	1.0	10	180	43.5	43	2230
0.4	1.0	10	180	51	50	1730
0.6	1.0	10	180	59	57	1550
0.8	1.0	10	..	67	..	1470
1.0	1.0	10	..	70	..	1220
1.2	1.0	10	..	77	..	1150
1.4	1.0	10	..	83	..	1080
0.4	0.4	60	..	86	..	1380
0.4	0.8	60	..	61	..	1540
0.4	1.0	60	..	51	..	1730
0.4	1.2	60	..	40	..	1610
1.0	0.8	30	..	82.8	..	1120
1.0	1.0	30	..	70.0	..	1220
1.0	1.2	30	..	62.5	..	1390
1.0	1.4	30	..	47.0	..	1280

\* Calculated as parts of active oxygen (equivalent weight = 8) per million parts of dry polymer.

*Effect of Phosphoric Acid in Preventing Interference by Antioxidant.* Experiments designed to increase the ease of oxidation of ferrous iron by lowering the ferrous-ferric ion oxidation potential were carried out. Fluoride and phosphoric acid were used as complexing agents. After preliminary experiments, phosphoric acid was adopted to avoid the etching effect of fluorides. The optimum concentrations of phosphoric and nitric acids were found by a study of the spectrophotometric absorption at 508  $m\mu$  of the ferrous and ferric *o*-phenanthroline complexes in the absence of peroxides. The same procedure was used as for ferrous and ferric complexes above, with the addition of phosphoric acid in the form of a methanol solution. The results appear in Table VI.

TABLE VI  
EFFECT OF PHOSPHORIC ACID

Con- centrated HNO <sub>3</sub> (cc.)	H <sub>3</sub> PO <sub>4</sub> (millimoles)	Time of standing		Transmission	
		t <sub>1</sub> (min.)	t <sub>2</sub> (min.)	I <sub>1</sub> (%)	I <sub>2</sub> (%)
On Ferrous Complex					
0.0	0.00	30	..	34	..
0.0	0.008	30	..	40.3	..
0.0	0.02	30	..	43.3	..
0.0	0.04	30	..	44.3	..
0.05	0.00	20	180	34.0	33.0
0.05	0.008	20	180	33.9	35.0
0.05	0.02	20	180	34.0	35.9
0.05	0.04	20	180	34.5	36.5
0.1	0.00	25	180	35	36
0.1	0.008	25	180	36	39
0.1	0.02	25	180	36	39
0.1	0.04	25	180	36	39
On Ferric Complex					
0.05	0.00	35	..	95	..
0.05	0.008	35	120	97	97
0.05	0.02	35	120	97	97
0.05	0.04	35	120	98	98



In each experiment 1.00 cc. of 0.002 *N* ferrous or ferric iron was treated with various amounts of phosphoric and nitric acids, *o*-phenanthroline was added, and the volume brought to 50 cc.

Even small amounts of phosphoric acid exert an adverse effect on the ferrous complex if no nitric acid is present, presumably by pulling the ferrous iron away from the *o*-phenanthroline complex. A small amount of nitric acid, by suppressing the ionization of the phosphoric acid, prevents the interference. Phosphoric acid has a desirable effect on the ferric iron in decreasing the absorption by forming the colorless ferric phosphate complex. From these results it was decided that 0.02 millimole of phosphoric acid and 0.05 cc. of concentrated nitric acid per 50 ml. are the optimum amounts.

To determine whether phosphoric acid prevents the interference by phenyl- $\beta$ -naphthylamine, the polymer solution containing antioxidant was tried with a reaction time of 20 minutes before adding the indicator. The results are shown in Table VII. A comparison of the results with those obtained with the same

TABLE VII  
OXIDATION OF FERROUS IRON IN PRESENCE OF ANTIOXIDANT

Polymer solution (cc.)	0.002 <i>M</i> ferrous iron (cc.)	Time after complexing (min.)	Transmission (%)	Active oxygen (p.p.m.)
0.2	1.0	15	44	2230
0.4	1.0	15	51.5	1770
0.6	1.0	15	59.2	1560
0.8	1.0	15	67	1420

polymer solution in the absence of antioxidant (Table V, first four experiments) shows that very similar data were found in the two cases. The modified method using both nitric and phosphoric acids was also tried on the polymer solution without antioxidant, with very similar results.

The commonly used antioxidants BLE (a complex condensation product of acetone and diphenylamine) and Stalite (an alkylated secondary arylamine) were likewise shown not to interfere in the peroxide determination.

#### ABSOLUTE ACCURACY

To check the absolute accuracy of the proposed method, an analysis of a standard peroxide was desired. Benzoyl peroxide and furoyl peroxide, which is much less stable thermally, failed to react noticeably with the reagent even after long standing. On the other hand, *tert*-butyl hydroperoxide reacted as readily as polymer peroxides.

Since Farmer and Sutton<sup>8</sup> have shown natural rubber peroxides to be of the hydroperoxide type, it was of interest to compare the results obtained on rubber peroxides by the proposed method and by the thiocyanate method of Robey and Wiese<sup>5</sup>, which responds to all peroxides. The same rubber or GR-S solution showed about 20 per cent more peroxide (relative) by the *o*-phenanthroline method than by the thiocyanate method.

Analysis of solutions of *tert*-butyl hydroperoxides standardized by the iodide method of Liebhaufsky and Sharkey<sup>10</sup>, and diluted for colorimetric analysis, showed that both colorimetric procedures gave high results, increasing with decreasing amounts of peroxide in the reaction mixture (compare Table V). However, careful exclusion of oxygen by bubbling the reagents before and

during the reaction led to lower results (Table VIII). With use of the thiocyanate method, the rate of reaction between peroxide and iron was found to decrease markedly as the last traces of oxygen were removed. Thus a fading of the thiocyanate color led to low results in air-free solutions. These observations suggest that peroxide catalyzes the air oxidation of iron (induced reaction) and conversely that oxygen catalyzes the peroxide iron reaction. Thus both colorimetric procedures are nonstoichiometric in the presence of air and very slow in its absence. For best results, both should be applied only over a narrow range of peroxide content in the reaction mixture.

TABLE VIII  
EFFECT OF AIR ON COLORIMETRIC PEROXIDE DETERMINATION

0.002 N peroxide (cc.)	0.002 N iron (cc.)	Iron used (cc.)	Recovery (%)	Conditions
<i>o</i> -Phenanthroline Method				
0.50	1.20	1.14	228	Air saturated
0.50	1.00	0.73	140	N <sub>2</sub> through benzene only
0.50	1.00	0.65	130	N <sub>2</sub> through all reagents before reaction
0.50	1.00	0.59	118	N <sub>2</sub> through all reagents and during reaction
Thiocyanate Method				
0.20	15	0.38	190	Air saturated
0.30	15	0.56	187	Air saturated
0.50	15	0.75	150	Air saturated
0.80	15	0.77	96	Air saturated
0.30	15	0.55	183	N <sub>2</sub> before reaction
0.50	15	0.72	144	N <sub>2</sub> before reaction
0.80	15	0.74	93	N <sub>2</sub> before reaction
0.30	15	0.18	60	N <sub>2</sub> before and during reaction
0.50	15	0.12	24	N <sub>2</sub> before and during reaction

If the recommended transmission range of 50 to 70 per cent is used in the proposed procedure (corresponding to a twofold range of peroxide concentration), comparative analyses can readily be made without standardization. For results of absolute significance, standardization by means of *tert*-butyl hydroperoxide is recommended. For larger amounts of peroxides, the iodide method gives stoichiometric results, but titration methods involving ferrous iron again were found to give high results in the presence of air. This observation has also been made by Kolthoff and coworkers<sup>11</sup> in the analysis of soap peroxides.

#### SENSITIVITY

The procedure as given is sensitive to 10 or 20 p.p.m. active oxygen, calculated on the solid polymer. No particular effort has been made to gain the utmost sensitivity, but much larger sample sizes could be used. The limiting factor is the color of the polymer solution itself, which could be compensated by using a solution of the polymer rather than benzene as the comparison liquid. By this means, less than 1 p.p.m. of active oxygen could be detected, considering the fact that the method gives an abnormal response to very small traces of hydroperoxide.

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## QUANTITATIVE DETERMINATION OF SOME INHIBITORS IN POLYMERS BY LIGHT ABSORPTION \*

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Organic polymeric substances are commonly subject to attack by atmospheric oxygen, which cause changes in the physical properties of the polymers. Inhibitors are usually incorporated to prevent or retard polymer degradation caused by atmospheric and imposed oxidizing conditions. The use of stabilizers is, therefore, very widespread and is especially important in synthetic rubbers.

Inhibitor concentration is an important factor in estimating the potential stability of a polymer. The concentration requirements for stabilizing polymers of different types vary with the type of polymer. The use of small concentrations of inhibitor has created an urgent need for a more precise method inhibitor analysis. Production control requires an easy and rapid method of analysis as well as accurate results, even where higher concentrations of inhibitor are used. *N*-Phenyl-2-naphthylamine (commonly called phenyl- $\beta$ -naphthylamine) has been used very widely in the stabilization of synthetic elastomers and, therefore, an effort was made to develop the best analytical method for this specific inhibitor. A method of analysis of primary aromatic amines involving titration with standardized nitrous acid<sup>1</sup> has been applied to its determination; however, when this method was used to determine the inhibitor present in a polymer in small concentrations, it was found unreliable in the absence of very careful control and expert manipulation. Craig<sup>2</sup> estimated the concentration of *N*-phenyl-2-naphthylamine in rubber by isolation of the hydrochloride. An adaptation of this method to Butyl rubber by a turbidimetric measurement of the amine hydrochloride has been used for production analysis but is unsatisfactory unless very careful control is maintained. An oxidative method using ceric sulfate has also been used with somewhat more reliable results. Investigation of rapid physical methods of analysis revealed that *N*-phenyl-2-naphthylamine has a very strong absorption in the near-ultraviolet region<sup>3</sup> which is very desirable for spectral analysis. Qualitative spectrographic determination of various rubber ingredients, including *N*-phenyl-2-naphthylamine, has been described<sup>4</sup>. The use of spectrophotometry now appears to be the best method of analysis for *N*-phenyl-2-naphthylamine in polymers.

Since polymers and various blending ingredients are not entirely transparent to ultraviolet light, it is necessary to subtract the "background" absorption (absorption due to materials other than *N*-phenyl-2-naphthylamine) to obtain a true estimation of inhibitor concentration in the polymer. A mathematical adaptation of the method which Wright<sup>5</sup> used in infrared spectroscopy in correcting for the background absorption, without actual measurement of

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the background absorption, was applied to this determination with considerable success. The method can be satisfactorily used with any polymer which can be dissolved in a solvent, or from which the inhibitor can be extracted by a solvent, where the background absorption is linear through the spectral points or wave lengths at which the inhibitor exhibits a maximum and two adjacent minimum absorptions. The correction for linear background absorption by optical density measurements at three wave lengths is outlined below. Although certain forms of this mathematical approach are in use, to the authors' knowledge it has not been previously reported. (Derivation and first application of this equation to polymer analysis was carried out in this laboratory by T. S. Chambers.)

Two assumptions are made: (1) Beer's law is obeyed and (2) the background absorption is linear with wave length over the portion of the spectrum involved. The former assumption has been found valid for the concentrations employed. Knowledge of the system used in the analysis will determine whether the latter is true or is a close approximation which would introduce but little error. Figure 1 is a typical illustration of the absorption of a solution of polymer containing an inhibitor.

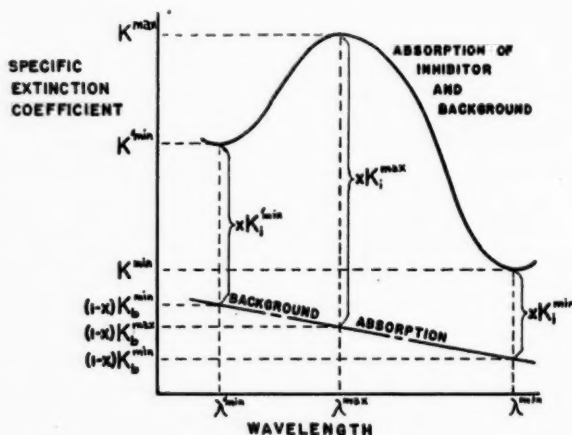


FIG. 1.—Typical Absorption of Solution of Polymer Containing an Inhibitor

$K'^{\min}$ ,  $K^{\max}$ , and  $K^{\min}$  are observed specific extinction coefficients of the polymer sample being analyzed for inhibitor content.  $K_b'^{\min}$ ,  $K_b^{\max}$ , and  $K_b^{\min}$  are the specific extinction coefficients of the background and  $K_i'^{\min}$ ,  $K_i^{\max}$ , and  $K_i^{\min}$  are the specific extinction coefficients for the inhibitor. Let  $x$  = fraction of inhibitor in polymer; and  $1 - x$  = fraction of polymer or background. Then

$$K'^{\min} = xK_i'^{\min} + (1 - x)K_b'^{\min} \quad (1)$$

$$K^{\max} = xK_i^{\max} + (1 - x)K_b^{\max} \quad (2)$$

$$K^{\min} = xK_i^{\min} + (1 - x)K_b^{\min} \quad (3)$$

The  $K$ 's and  $K_i$ 's are experimentally determined, leaving four unknowns. The value of  $x$  can be determined without knowing  $K_b$ 's if one of the  $K_b$ 's is

known in terms of the others. From Figure 1:

$$(1 - x)K_b^{\max} = (1 - x)K_b^{\min} + \frac{\lambda_{\min} - \lambda_{\max}}{\lambda_{\min} - \lambda'_{\min}} [(1 - x)K_b'^{\min} - (1 - x)K_b^{\min}] \quad (4)$$

or

$$K_b^{\max} = (1 - n)K_b^{\min} + nK_b'^{\min} \quad (5)$$

where

$$n = \frac{\lambda_{\min} - \lambda_{\max}}{\lambda_{\min} - \lambda'_{\min}} \quad (6)$$

Substitute values of  $K_b'^{\min}$  and  $K_b^{\min}$  from Equations 1 and 3 in Equation 5:

$$K_b^{\max} = \frac{(1 - n)(K_i^{\min} - xK_i'^{\min}) + n(K_i'^{\min} - xK_i'^{\min})}{1 - x} \quad (7)$$

Substitute value of  $K_b^{\max}$  from Equation 7 in Equation 2:

$$x = \frac{K_i^{\max} - (1 - n)K_i^{\min} - nK_i'^{\min}}{K_i^{\max} - (1 - n)K_i^{\min} - nK_i'^{\min}} \quad (8)$$

Since  $K = \frac{D}{LC}$

where  $D = \text{optical density} = \log \frac{I_{\text{solvent}}}{I_{\text{solution}}}$

$L = \text{cell length} = 1 \text{ cm.}$

$C = \text{concentration of polymer in solution in grams per liter}$

$I_{\text{solvent}} = \text{intensity of light through pure solvent}$

$I_{\text{solution}} = \text{intensity of light through polymer solution}$

then

$$\% \text{ inhibitor in polymer} = \frac{100[D^{\max} - (1 - n)D^{\min} - nD'^{\min}]}{C[K_i^{\max} - (1 - n)K_i^{\min} - nK_i'^{\min}]} \quad (9)$$

### EXPERIMENTAL

The choice of solvent should be such that it will dissolve both polymer and inhibitor, and it must be easily obtained in a pure state and preferably show low and linear absorption in the spectral region employed. Ethylene dichloride and chloroform are satisfactory solvents for GR-S and Perbunan. These solvents as well as carbon tetrachloride and isoöctane are suitable solvents for Butyl rubber.

A Beckman quartz prism spectrophotometer<sup>6</sup> with a hydrogen discharge tube serving as the light source was used for all optical density measurements. Quartz cells with a light path of 1 cm. held the liquid samples.

Extinction coefficients of the inhibitors in the solvents to be used for the analyses were determined by optical measurements at the wave lengths of the maximum and two adjacent minimum absorptions best suited for analytical purposes. Several concentrations were employed and an average extinction coefficient was calculated for the inhibitor at each of the three wave lengths. It is important that measurements of extinction coefficients of inhibitors be made for each instrument, since the exact dispersion, resolving power, actual slit width, photocell spectral sensitivity, and amount of reflected and scattered



light of the instrument are factors which affect the optical density measurements.

Since only small samples of polymer were employed, care was exercised to get truly representative results. This was accomplished by milling and refining a sample of rubber from which portions were taken for analyses. Milling was also beneficial in destroying gel in polymers which would introduce error from light reflection. Excessive milling and heating in contact with air were avoided.

An accurately weighed portion of polymer was placed in a glass-stoppered Erlenmeyer flask and a known volume of solvent added from a pipet. Dissolution occurred on standing 1 or 2 days with occasional shaking, or it was accelerated by stirring or heating. A clear sample was removed from any settled insoluble material (centrifuging may be used) and transferred to the quartz cell for optical density measurements. A matched quartz cell containing a solvent control was used as the reference zero optical density. The concentration of inhibitor in the polymer was calculated by means of Equation 9. Using this procedure, only a few minutes are required to determine the inhibitor content of a sample of dissolved polymer.

TABLE I  
SPECIFIC EXTINCTION COEFFICIENTS OF *N*-PHENYL-2-NAPHTHYLAMINE  
AND UNINHIBITED POLYMERS

Wave length (mμ)	Specific extinction coefficients, <i>K</i> (l. g. <sup>-1</sup> cm. <sup>-1</sup> )				
	PBN in isoöctane	Butyl rubber in isoöctane	PBN in C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	GR-S in C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	Perbunan in C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>
282	49.7	0.01-0.06	54.0	..	..
284	52.0	..	51.5	0.05	0.03
308	85.6	.01-0.04	85.0	..	..
309	83.5	..	87.0	0.04	0.02
326	13.2	0.01	17.0	..	..
332	15.0	..	15.0	0.01	0.01

#### DISCUSSION

The specific extinction coefficients of *N*-phenyl-2-naphthylamine showed slight variation in numerical value and spectral position with the solvent employed. The evaluation of the coefficients used in calculations in this paper are given in Table I and their use permits simplification of Equation 9 to the following expressions:

$$\% \text{ PBN in Butyl rubber} = (D^{308} - 0.6D^{326} - 0.4D^{282}) \frac{1.73}{C} \quad (10)$$

$$\% \text{ PBN in Perbunan and GR-S} = (D^{309} - 0.52D^{332} - 0.48D^{284}) \frac{1.83}{C} \quad (11)$$

where the solvent for Butyl rubber is isoöctane and that for Perbunan and GR-S is ethylene dichloride. Solutions containing about 0.01 gram of *N*-phenyl-2-naphthylamine per liter (or about 0.3 gram of Butyl rubber or 0.05 gram of Perbunan or GR-S per 100 ml.) were most satisfactory for optical density measurements with the Beckman instrument. These solutions have optical densities in the range of 0.1 to 1.0 for the wave lengths prescribed.

The advantage of the ultraviolet absorption method for the determination of *N*-phenyl-2-naphthylamine in Butyl rubber as compared with the turbidim-

etric determination by precipitated hydrochloride is evident from Table II. An oxidation method involving ceric sulfate oxidation of the inhibitor gave results in good agreement with those obtained by the ultraviolet method.

The calculation of inhibitor content by using only the wave length of maximum absorption gives values listed in Table II as uncorrected for background. This calculation represents the maximum amount of inhibitor that can be in the polymer and is made by Equation 12:

$$\text{Maximum possible \% PBN in polymer} = \frac{100K^{308}}{K^{308}} = 1.17 \frac{D^{308}}{C} \quad (12)$$

The uncorrected value does not always agree with that corrected for background absorption but tends to be higher where the background absorption is greater.

TABLE II  
COMPARISON OF METHODS OF ANALYSIS OF BUTYL RUBBER FOR  
*N*-PHENYL-2-NAPHTHYLAMINE

Polymer composition	% <i>N</i> -phenyl-2-naphthylamine in polymer			
	Chemical methods		Ultraviolet method	
	Hydrochloride turbidimetric	Ceric sulfate	Corrected for background	Uncorrected for background
Pure Butyl rubber	0.00	..	0.00	0.01
Pure Butyl rubber + 0.25% PBN <sup>a</sup>	0.22	..	0.24	0.26
Pure Butyl rubber + 2.5% zinc stearate <sup>a</sup>	0.00	..	0.00	0.03
Pure Butyl rubber + 2.5% zinc stearate + 0.25% PBN <sup>a</sup>	0.40	..	0.23	0.26
Butyl rubber (light colored)	0.63	0.35	0.35	0.41
Butyl rubber (dark colored)	0.48	0.00	0.00	0.09
Butyl rubber (dark colored) + 0.25% PBN <sup>a</sup>	0.42	0.25	0.21	0.33

<sup>a</sup> Added on mill.

The dark-colored Butyl rubber sample in Table II showed no inhibitor present by corrected ultraviolet analysis, while the uncorrected analysis indicated that inhibitor was still present. Storage stability of this polymer was very poor, indicating that inhibitor was absent.

From a large number of inhibitor determinations on Butyl rubber containing about 0.25 per cent *N*-phenyl-2-naphthylamine, the following probable errors were obtained when corrected for background absorption:

Mean deviation from theoretical	±0.01% PBN
Maximum deviation from theoretical	±0.04% PBN
Mean reproducibility	±0.01% PBN
Maximum deviation from mean	±0.04% PBN

The ultraviolet absorption of GR-S and Perbunan polymers which contain small amounts of such impurities as hydroquinone, soap, fat acid, persulfate, and thiol is very low compared to that of *N*-phenyl-2-naphthylamine. Since larger amounts of antioxidant are used in the Buna-type polymers (about 2.0 per cent) than in Butyl rubber (about 0.25 per cent), the background ab-

sorption of unaged Buna-type polymers is of less significance in determining the inhibitor contents of the polymers by ultraviolet absorption. It is then usually necessary to measure the absorption of a polymer solution only at the wave length of maximum absorption (309  $m\mu$ ) and calculate the inhibitor concentration by Equation 13.

$$\text{Maximum possible \% PBN in Perbunan or GR-S} = \frac{100K^{309}}{K_s^{309}} = 1.15 \frac{D^{309}}{C} \quad (13)$$

Even fresh polymers may, however, become contaminated with impurities by milling or improper washing, so that the magnitude of the background absorption is increased, thereby making a background correction necessary if accurate and reproducible results are required. In Table III data are presented illustrating the application of ultraviolet absorption and Equations 11 and 13 to the determination of *N*-phenyl-2-naphthylamine in Buna-type polymers. In certain cases the antioxidant was extracted from the polymers with glacial acetic acid and the extracts titrated with nitrous acid to starch-iodide end points. In these cases special precautions were taken to obtain complete extraction and avoid losses which generally accompany this type of analysis.

TABLE III  
COMPARISON OF DIFFERENT METHODS OF ANALYSIS OF BUNA-TYPE  
POLYMERS FOR *N*-PHENYL-2-NAPHTHYLAMINE

Polymer composition *	% <i>N</i> -phenyl-2-naphthylamine in polymer		Chemical method, nitrous acid titration of HOAc extract
	Corrected for background	Uncorrected for background	
Unstabilized Perbunan	0.00	0.02	0.00
Perbunan + 1.9% PBN added on mill (A)	1.91	1.99	..
Perbunan (A) milled 10 minutes at 20° C	1.88	1.96	..
Perbunan (A) milled 10 minutes at 100° C	1.80	1.96	..
Perbunan (A) aged 4 days, air oven, 85° C	1.79	1.87	..
Perbunan + 2.0% PBN added on mill (B)	1.98	2.05	1.91
Perbunan commercial product (C)	1.64	1.69	1.65
Perbunan (C) aged 46 days, air oven, 60° C	1.32	1.42	..
Perbunan, dark colored stock	1.85	2.26	..
Unstabilized GR-S	0.00	0.05	..
GR-S + 0.5% PBN added on mill (A)	0.51	0.54	0.58
GR-S + 1.96% PBN added on mill (B)	1.96	1.99	1.98
GR-S (B) aged 46 days, air oven, 60° C	0.74	1.24	..

\* Parenthetical letter refers to specific polymer-inhibitor compositions.

Data are also presented in Table III to show the effect of natural and imposed oxidizing conditions on the antioxidant contents of polymers. Ultraviolet analyses of such polymers show not only decreased amounts of antioxidant present in the aged polymers, but also a variation in the two methods of calculation (Equations 11 and 13) which can be accounted for only by assuming that oxidation products of the inhibitor and polymer are contributing to the background absorption.

Inspection of the absorption spectra of highly oxidized Perbunan and GR-S polymers reveal that the characteristic peak absorption of the *N*-phenyl-2-naphthylamine at 309  $m\mu$  has been at least partially destroyed, and the absorption has become more linear with wave length than is the case for the absorption of the pure inhibitor. Under such circumstances, application of a

background correction results in much more accurate evaluations of the inhibitor contents of the polymers than either measurement of the optical density of the polymer solution at only one wave length, or application of analytical procedures which depend on the reaction of a functional group of the inhibitor. The nitrous acid titration procedure, for example, fails to distinguish oxidation products of *N*-phenyl-2-naphthylamine from the pure inhibitor if amine groups are present in the oxidation products and if these groups form nitroso derivatives. The work of Rehner, Banes, and Robinson<sup>7</sup> has demonstrated that amine compounds may occur in oxidation products of *N*-phenyl-2-naphthylamine.

The changes in ultraviolet absorption and inhibitor content of Perbunan and GR-S polymers due to oxidation promoted by heat and light are further illustrated in Table IV. The more probably correct analyses are those obtained where background corrections have been made.

TABLE IV  
EFFECT OF AGING OF BUNA-TYPE POLYMERS ON ULTRAVIOLET  
ABSORPTION AND INHIBITOR ANALYSES

Polymer	Aging conditions	Optical density			Concn. (g. per l.)	% <i>N</i> -phenyl-2-naphthylamine in Polymers		
						Ultraviolet method		Chemical method, nitrous acid titration of HOAc extract
		284 mμ	309 mμ	332 mμ		Corrected for back- ground	Uncor- rected for back- ground	
Perbunan	Original	0.447	0.732	0.136	0.500	1.64	1.69	..
	50 days, air oven, 82° C	0.206	0.313	0.076	0.500	0.27	1.05	..
GR-S	Original	0.485	0.805	0.148	0.500	1.81	1.85	1.82
	50 days, air oven, 82° C	0.360	0.333	0.117	0.500	0.36	0.77	0.43
GR-S	Original solu- tion	0.158	0.878	0.545	0.500	1.96	2.02	..
	Same solution aged 10 days in diffused sunlight at room tem- perature	0.202	0.716	0.642	0.500	1.11	1.65	..

This method of analysis has been extended to other inhibitors. It is most reliable where large values for maximum extinction coefficients are encountered. The wave lengths which were used for analyses for certain of these inhibitors in polymers are shown in Table V.

TABLE V  
WAVE LENGTHS APPLICABLE FOR ULTRAVIOLET DETERMINATION  
OF INHIBITORS

Inhibitor	Solvent	Wave lengths in mμ for		
		λ <sub>min</sub>	λ <sub>max</sub>	λ <sub>min</sub>
Aminox <sup>a</sup>	Ethylene dichloride	246	291	355
Agerite Stalite <sup>a</sup>	Ethylene dichloride	251	286	353
Inhibitor 8567 <sup>a</sup>	Isooctane	246	277	300
<i>N</i> -Phenyl-2-naphthylamine	Isooctane	282	308	326
<i>N</i> -Phenyl-2-naphthylamine	Ethylene dichloride	284	309	332
<i>N</i> -Phenyl-2-naphthylamine	Chloroform	284	309	332

<sup>a</sup> Aminox, amine-ketone condensation product. Agerite Stalite, alkylated aromatic amine. Inhibitor 8567, phenolic type.

## SUMMARY

A spectrophotometric method of analysis for inhibitors in polymers has been developed. This method corrects for background absorption and has been found to be rapid and more reliable than chemical methods of analyses which were investigated.

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# THE PREPARATION OF POSITIVE LATEX \*

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## INTRODUCTION

Under normal conditions the particles of Hevea latex, whether or not the latex happens to be fresh or preserved, carry a negative electric charge. Several authors have called attention to the practical interest which there might be in a latex having positively charged particles. Blow<sup>1</sup>, for example, has shown that textile fibers can be impregnated very satisfactorily when their electric charge is the opposite of that of the latex particles. In the case of wool, this means the use of positive latex in an alkaline medium. Under these conditions it is necessary to reverse the charge of ordinary latex, and in doing this, certain problems, both theoretical and practical, are encountered.

In the present work two subjects are first of all discussed: (1) the theoretical point of view, *i.e.*, the origin, changes in the electric charge, and the stability of the latex; and (2) different methods which have been described in the literature for reversing the charge of fresh and preserved latex, and the results obtained. In addition to this discussion, some experiments with these methods, and processes which have given the best results, are described.

## THE THEORETICAL POINT OF VIEW

### ORIGIN AND REVERSAL OF THE CHARGE

The electric charge on latex particles and, in general, on the majority of colloidal dispersions has its origin in the ionization of one or several substances adsorbed on the surface of the particles. These substances, which function as stabilizing or peptizing agents, are, in ordinary latex, protein by nature, and they contain at the same time weak basic groups (amino groups) and weak acid groups. The ionization varies greatly with the pH value. In an alkaline medium the acid groups are ionized, whereas the amino groups are not; the resultant charge is negative. In an acid medium the opposite charge prevails, for only the amino groups are dissociated; hence the charge is positive<sup>2</sup>. There is an intermediate pH value at which ionization of the two groups is equivalent; the resultant charge is then zero. This pH value, the isoelectric point of the dispersion, is different from the pH value at the neutral point, for the ionogenic groups are not equally powerful. In latex this point is at a pH value of approximately 4.5.

By changing the pH value, it is possible to change the sign of the charge on the particles and to obtain a positive acidic latex or a negative alkaline latex.

Another method for changing the electric charge is available. It has just been mentioned that latex particles may be regarded as being covered with positive and negative ions, whereby the actual charge is determined by the predominant ion. If ions of a definite sign are added, the charge is altered.

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Ions in solution, in the serum are in part adsorbed in the particles, and the extent of this adsorption depends on several factors: (1) the sign of the ion; positive ions are most easily adsorbed on the negative particles; (2) the valence; polyvalent ions are strongly adsorbed; (3) the molecular mass.

There are several important results of this adsorption. First of all it makes it possible to explain the influence of electrolytes which are naturally present in latex. These electrolytes contribute to the partial discharge of the particles, regardless of their sign, and thus reduce the stability of the particles. This is a major inconvenience when it is necessary to have maximum stability, which is the case in reversion. These electrolytes are chiefly alkaline salts, and although their effect on the electric charge is considerable<sup>3</sup>, they neither nullify the charge nor change its sign. On the contrary, when salts having polyvalent cations are added to latex, there is an appreciable decrease in the electric charge, and at a certain concentration the charge reverses. Tetravalent cations, above all thorium, *e.g.*, thorium nitrate, are particularly effective.

In spite of this, the use of these salts cannot in general be recommended, chiefly because of the deleterious effect of heavy metals on the aging of rubber. On the contrary, cationic soaps appear to be much more interesting. Ordinary types of soap, *e.g.*, alkaline oleates and stearates, give by dissociation active anions. These are anionic soaps, and they are stabilizing agents for negative dispersions. Cationic soaps give, by dissociation, active cations. These are salts of organic bases substituted by a long chain hydrocarbon. Recently these products have appeared commercially.

Soaps alter the charge of latex particles without changing the pH value or the ionization of the protein layer. The isoelectric point is displaced toward high acidities by anionic soaps and toward high alkalinities by cationic soaps<sup>4</sup>.

In brief, then, reversion can be effected by any of three general methods: (1) by changing the pH value; (2) by changing the isoelectric point (by cationic soaps); (3) by the combined use of methods (1) and (2).

#### STABILITY OF LATEX. COAGULATION

Methods for changing the charge on latex particles have been pointed out, but no mention has been made of the effect produced in the latex itself by such a change.

The stability of latex is attributable, in great part, to the electric charge on its particles. At the isoelectric point, for example, coagulation takes place, but it is not necessary for discharge to be complete, and coagulation takes place in a critical zone of charges lying on each side of zero charge. Whatever the method of reversion, latex remains for a certain time in this critical zone, with coagulation taking place to a certain extent. For reversion to be possible, this coagulation must be negligible. Actually it takes place at a rate which depends on several factors: (1) the rate of passage through the critical zone (it is necessary to add compounding ingredients rapidly); (2) electrolytes present in the latex which act by buffering the charge around the isoelectric point and increasing thereby the time of passage through the critical zone; and (3) the concentration (the rate of coagulation is proportional to the concentration). By dilution the rate of coagulation and the concentration of electrolytes are reduced.

Another factor which increases the rate of coagulation and which it is impossible to control in any direct way is the deterioration of the natural stabilizing agent present in latex. This influence is particularly evident in the

case of preserved latex. The rate of coagulation can be diminished during passage through the critical zone by the addition of a suitable stabilizing agent, *e.g.*, casein.

#### DIFFERENT METHODS OF REVERSION

##### REVERSION OF FRESH LATEX

It has been known for a long time that the addition of an excess of acid does not accelerate the coagulation of fresh latex; on the contrary it retards coagulation and leaves it incomplete. In the case of dilute latex, coagulation can even be prevented altogether. This phenomenon, designated as the gap or second liquid zone, has for a long time remained without any satisfactory explanation, and the various theories of coagulation are at variance with the phenomenon<sup>5</sup>.

As long ago as 1923, Belgrade observed that latex particles in the second zones are charged positively<sup>6</sup>. A few years later, several investigators determined the limits of stability of latex in the second zone diluted to one-tenth its concentration) 1 part of fresh latex and 9 parts of water); they found<sup>7</sup> as the upper limit a pH value of 3.5 and as the lower limit a pH value which varied from 0.80 to 1.

Fullerton<sup>8</sup> studied the changes in these limits of stability as a function of the concentration of latex. He was not able to obtain stable positive latex above 15 per cent concentration (with limits of stability of 3 and 1.25, respectively). On the other hand, Rhodes succeeded in obtaining stable acid latex of 30 per cent concentration<sup>9</sup>.

Unlike fresh latex, acid latex does not ferment; spontaneous coagulation does not take place, and at one time it was even thought that acidification might offer a means of preserving latex<sup>9</sup>.

Unfortunately, however, acidic positive latex is not very stable, either chemically or mechanically, and vigorous agitation brings about coagulation. The only attempt to stabilize acid latex prepared from fresh latex has been described by Rhodes and Sekar<sup>9</sup>, who added 1 per cent of saponin (based on the rubber phase).

The literature does not seem to mention any attempts to bring about reversion by cationic soaps.

De Vries studied the properties of rubber obtained from positive latex, and found that it had different properties from those of ordinary rubber. In particular it was more plastic<sup>10</sup>.

##### REVERSION OF PRESERVED LATEX

From the viewpoint of practical interest, the treatment of preserved latex is of much more concern to the consumer far from the plantations. Unfortunately it is a delicate operation to bring about reversion, chiefly for two reasons: (1) the presence of a stabilizing agent, and (2) the variability of preserved latex.

*Presence of a stabilizing agent.*—Ammonia, which is the most widely used agent, has one great fault when the aim is to make latex positive; it necessitates the addition of a greater quantity of acid to lower the pH value to the correct point; moreover, it forms ammonium salts which buffer the solution and prevent the obtaining of a sufficiently low pH value. In addition, these ammonium salts are electrolytes, the harmful effects of which have already been pointed out.

Other stabilizing agents which have been used, all of which are alkaline, have the same faults.

Ammonia must, then, be eliminated from the latex to be treated, to which end several methods are available.

(1) The simplest method is to neutralize the ammonia, without at the same time forming an electrolyte. Formaldehyde gives excellent results; it reacts with ammonia to form hexamethylenetetramine. It is necessary to avoid an excess of formaldehyde, for this may react with the proteins of the latex. It is quite safe, however, to lower the pH value from 10-10.5 to 7.

The use of carbon disulfide has been mentioned as a neutralizing agent for the ammonia, but it would tend to form accelerators of vulcanization.

(2) In industry, a method frequently used is to remove the ammonia by a current of a gas. Various modifications of this method have been utilized, such as a current of air or of an inert gas, *e.g.*, nitrogen, while heating the latex or atomizing the latex in the gas current to accelerate the elimination of ammonia.

(3) Finally there is the method of dialysis. This process has for a long time been confined to the laboratory; however, an industrial technique has been described by Stevens, Dyer and Rowe<sup>11</sup>. Although it is more delicate than the other two methods, dialysis has the great advantage of eliminating the electrolytes at the same time that it does the ammonia.

*Variability of preserved latex.*—The addition of ammonia to latex brings about two types of transformations; first of all rapid changes, becoming evident in a few days, which serve to distinguish fresh latex from preserved latex, and which are manifest in a decrease in viscosity, an increase in chemical and mechanical stability, and an increase in resistance to fermentation; and secondly slow changes, probably attributable to the progressive degradation of proteins resulting from the alkalinity of preserved latex. These latter slow changes are manifest in a slow decrease in stability<sup>12</sup> and by profound changes in the behavior of the latex. This phenomenon seems to have been disregarded by many investigators, and it may explain the contrary results to be found in the literature. Fullerton, for example, working on the plantation with freshly preserved latex, had no difficulty in bringing about reversion, whether the latex had been treated with ammonia or with soda. The limits of stability at different concentrations were essentially the same as those of fresh latex. He found, however, that latex to which soda had been added changed with time, and that after long storage it could not be acidified without coagulation taking place. On the other hand, with latex containing ammonia, it was possible to bring about reversion, even after storage.

It does not seem, however, as if his tests could have been continued for a very long time, for other investigators, who studied preserved latex, not on the plantation but at the places where it was to be used in manufacture, were not able to bring about reversion directly.

The essential difference between fresh latex and preserved latex is that the latter shows a very high rate of coagulation in the critical zone. The addition of acid brings about local coagulation before the acid has had time to be distributed throughout, and this is the principal difficulty involved in the reversion process.

*Reversion by cationic soaps.*—Investigations of Blow<sup>13</sup> have shown the possibility of preparing positive latex with the aid of cationic soaps. However, even before the work of Blow, Elkington<sup>14</sup> had described the use of similar agents. As stabilizing agents for positive latex, he made use of basic dyes,

such as methylene blue. These compounds have structures analogous to the cationic soaps of Blow.

According to Blow, the minimum quantities (expressed as percentage by weight of the actual rubber) of cationic soaps, *e.g.*, Fixanol and cetyltrimethylammonium bromide, to add to 5 per cent latex to bring about reversion are: for ordinary dialyzed latex, 6; centrifuged latex, 7; Revertex, above 20; creamed latex, above 14; creamed dialyzed latex, 10; centrifuged vulcanized latex, 15; centrifuged vulcanized dialyzed latex, 9.5; triple centrifuged latex, 5.5.

More recently Coplan, Rogers and Hansen<sup>15</sup> succeeded in preparing a positive 20 per cent latex by pouring the latex into a 5 per cent solution of a cationic soap. The latex used in this case had been concentrated by centrifugation. These investigators used 5 per cent of stabilizing agent, and they obtained a positive latex which was unstable when the pH values were alkaline but was stable after the pH value was lowered by acetic acid to approximately 4.

*Reversion by changing the pH value.*—The results obtained by this method differ greatly according to the different investigators who have worked on the problem. It has already been mentioned that Fullerton<sup>8</sup> succeeded in bringing about the reversion of preserved latex. It has likewise been stated in other works<sup>16</sup> that a stable dispersion is obtained by the rapid addition of a sufficient quantity of acid to latex. Nevertheless, the majority of such attempts have failed, probably because of degradation of the proteins. The next efforts were to stabilize latex before reversion by an agent which is without influence on the isoelectric point. Several patents have utilized this method<sup>17</sup>, but in general they give only practical information. The stabilizing agents which have been recommended include proteins (casein, hemoglobin, albumin, gelatin, etc.) and glucosides (saponin, arbutin, etc.). Anionic soaps are not mentioned.

#### ARTIFICIAL POSITIVE DISPERSIONS

*Dispersions of natural rubber.*—It is now known how, by various methods, to redisperse coagulated rubber. All methods give negative dispersions. When it is desired to obtain artificial positive latices, it is evident that the same methods of reversion used for natural latex are applicable to these artificial dispersions. However, it would seem to be simpler to modify the way of preparing the dispersion so as to obtain positive latex directly.

The two general methods of dispersion can be utilized for this purpose: (1) to prepare a solution of rubber in an organic solvent, in an aqueous solution of a cationic soap (at any pH value) or in an acidic solution of casein<sup>18</sup>; or (2) as an alternative, to make the dispersion on a mill<sup>19</sup>.

*Dispersion of artificial rubber.*—These dispersions are obtained directly by polymerization in emulsion. In general, anionic soaps are utilized as emulsifying agents, in which case negative latices are obtained. It should be easy, by using a cationic soap as the emulsifying agent, to obtain positive latices.

#### EXPERIMENTAL RESULTS

Attempts to bring about reversion in latex in the laboratory, have given much less satisfactory results than those described in the literature. The various investigators who have studied this problem seem to have disregarded one very important factor, *viz.*, the lengths of time that their latices had been preserved. In general, the investigations were carried out on latices which had been shipped for industrial use, and which had been preserved at least for

several months. Because of untoward events, the only latex available for experimentation by the present author had been preserved for at least two years, and the results obtained with it show the very great influence of the time of preservation.

*Reversion by change in the pH value.*—When no stabilizing agent was present, latex coagulated completely, whatever the quantity of acid added and the rate of this addition. Purification of latex by dialysis did not improve conditions appreciably, any more than did dilution; even 1 per cent latex coagulated completely.

On the contrary, the addition of stabilizing agents gave better results, although still far from perfect. Not all the agents which have been described in the literature were found to be suitable. Casein and hemoglobin gave excellent results, and casein should find industrial applications; other proteins, such as albumin and gelatin, were without effect. Glucosides such as saponin also were ineffective. The stabilizing action was not manifest immediately after addition of the agent, but required a certain time of standing, of the order of 24 hours.

A suitable proportion of stabilizing agent was about 2 per cent of the rubber, and higher percentages were of no advantage. In this proportion, latex up to 5 per cent concentration was stabilized successfully.

Ordinary ammoniated latex may be chosen as an example. In this case 2 per cent (by weight of the rubber) of an ammoniacal solution of casein was added to the latex, the mixture was allowed to stand for 24 hours, was then diluted to 5 per cent concentration, and the ammonia was neutralized by formaldehyde to a pH value of 7. Sufficient acetic acid was then added to lower the pH value to 3. This acetic acid should be added at one time in the form of concentrated (40 per cent) acid, and with vigorous mechanical agitation.

It has already been pointed out that anionic stabilizing agents cannot be used. However, it is well to mention a special case, that of Igepon-T. After stabilizing undiluted latex by the addition of 5 per cent of this agent, it was possible to treat the latex with half its volume of concentrated hydrochloric acid without coagulation taking place. In this way there was obtained a positive latex containing 20 per cent of rubber, with a concentration of hydrochloric acid of 3 to 4 normal. This treated latex was very stable, but it coagulated when the concentration of the hydrochloric acid was decreased by any means whatsoever, *e.g.*, by partial neutralization or by simple dilution. It might be thought that this reversion could be attributed to the constitution of Igepon-T, which is oleylmethyltaurine,  $C_{17}H_{33}CONMeC_2H_5SO_3Na$ , and which, by virtue of its amide group, should behave as an amphoteric compound, whose isoelectric point lies in a very acid pH range, *viz.*, close to zero.

*Stabilization of acid positive latex.*—The addition to acidic latex of a certain quantity of a positive soap increased the stability of the latex. By the addition of 2 per cent (based on the rubber content) of Soromine-BS, it was possible to increase the concentration by 5 per cent. It was found to be of advantage to add the stabilizing agent at the same time as the acid, in every case with good mechanical agitation.

*Reversion by cationic soaps.*—With cationic soaps, the effect of stabilization was particularly evident. Trials of the methods of Blow<sup>13</sup> and of Coplan, Rogers and Hansen<sup>15</sup> were conclusive. According to Blow, 5 per cent latex undergoes reversion when a cationic soap, the quantity depending on the particular latex, is added. Nevertheless, when even more than 20 per cent of Soromine-BS was added, a stable latex could not be obtained. Ordinary



coagulation did not take place, but in every case the latex flocculated irreversibly.

The procedure described by Coplan, Rogers and Hansen<sup>15</sup> calls for adding 20 per cent latex to a 5 per cent solution of soap, and then acidifying for stabilization. In all cases coagulation took place as soon as the acid was added. The coagulum obtained was soft and weak. In these tests Soromine-BS and Sapamine-FL were used as stabilizing agents. The latices which were tested included ordinary ammoniated latex, ammoniated creamed latex, and centrifuged latex. All behaved in the same way.

### CONCLUSIONS

In the reversion of the electric charge of latex particles, certain difficulties are encountered which have not been pointed out by various other investigators who have published work on the subject.

With preserved latex in the form that it is received in consumer countries, it can hardly be hoped to obtain stable dispersions of even fairly high concentrations, unless the latex is shipped and delivered within a very short time. An interesting solution of this problem would be the preparation of positive latex directly on the plantations. Here the use of cationic soaps would make it possible to obtain still better results than have already been attained.

Finally, attention should be called to the fact that certain types of latex other than that of Hevea, in particular *Funtumia elastica* latex, seem to show considerably greater stability with change in their pH values. These latices are, of course, not yet used industrially, but present developments in African rubbers might change this situation. The use of such latices would then be advisable in certain cases<sup>20</sup>, particularly in problems such as the one just discussed, the preparation of positive latex.

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# MOLECULAR FRACTIONATION BY DIFFUSION OF GUAYULE AND CRYPTOSTEGIA RUBBER \*

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While it has been known for many years that guayule rubber obtained from two-year-old shrubs<sup>1</sup> is inferior in most of its physical properties to Hevea rubber, it has also been known that *Cryptostegia*, which can be tapped one year after planting, yields a high quality rubber<sup>2</sup> which compares reasonably well with smoked sheet or crepe.

Combustion analysis indicated that both are built up from the same building unit as Hevea rubber and their x-ray diffraction patterns (Figures 1, 2 and 3) also support this assumption. All three can be classified as polyisoprenes.

Although a systematic study of the chemical composition of guayule rubber revealed that its deficiencies were mainly due to the presence of resin and not to the composition of the hydrocarbon, it must be admitted that a detailed evaluation of its physical properties in regard to modern compounding techniques revealed results which were at variance from those reported earlier<sup>3</sup>.

This variation may be ascribed to the source and pretreatment of the guayule as well as its sensitivity to oxidation, aging, vulcanizing and milling temperatures. It is also logical to assume that the age of the plant from which the rubber was obtained might enter in the picture.

In all cases, however, it was found that the physical properties of guayule-carbon black compounds could not be compared with those obtained from Hevea. This fact, together with observations on the behavior of guayule when subjected to milling, seemed to indicate that the difference in physical properties of Hevea and guayule might be explained by assuming that their average molecular-chain length and size distribution differ.

The physical properties of *Cryptostegia* rubber approached more closely those of Hevea rubber. *Cryptostegia* also did not seem to be as sensitive in regard to storage conditions.

Qualitative experiments showed that, whereas guayule is practically soluble in customary rubber solvents, *Cryptostegia* shows a considerable amount of insoluble gel rubber.

Therefore it seemed appropriate to study systematically the molecular size and weight distribution of guayule as well as *Cryptostegia* rubber. In the case of guayule, it was also thought of interest to study the effect of resin extraction and the influence of the various solvents used for this purpose.

Diffusion fractionation was carried out in hexane following the suggestion of Kemp and Peters<sup>4</sup> to use a "poor solvent" to obtain closer fractionation.

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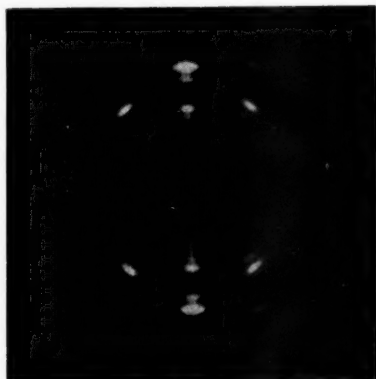


FIG. 1.—X-ray Diffraction Pattern of Hevea Brasiliensis Rubber

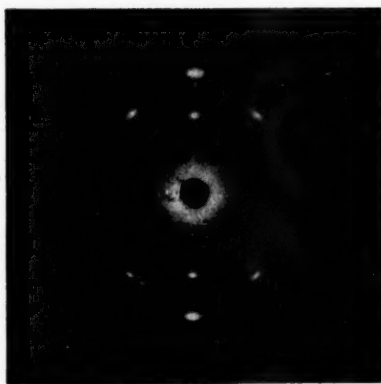


FIG. 2.—X-ray Diffraction Pattern of Guayule Rubber

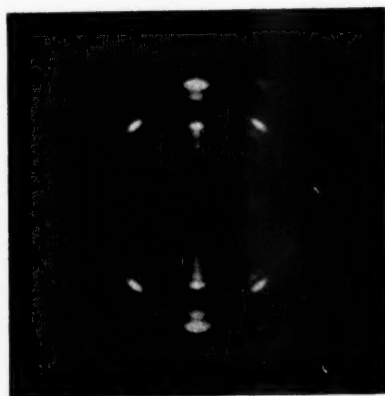


FIG. 3.—X-ray Diffraction Pattern of Cryptostegia Grandiflora Rubber

For reasons previously discussed<sup>5</sup> the calculations of the molecular weight were carried out according to Arrhenius' equation. Since both guayule and *Cryptostegia* have the same chemical composition and show identical x-ray diffraction patterns, it seemed logical to apply the same constant for the calculation of the molecular weight as for *Hevea* rubber<sup>6</sup>.

It also seemed appropriate to study the morphology of rubber molecules by applying the recently developed microscopic technique using ultraillumination by incident light<sup>6</sup>.

#### FRACTIONATION AND MOLECULAR WEIGHT DETERMINATION OF *CRYPTOSTEGIA*

Water-coagulated *Cryptostegia* rubber was subjected to exhaustive acetone extraction at room temperature before fractionation to remove the resin. The rubber was then dried in a vacuum and placed in hexane (b.p. 60–70° C) in a cotton bag and subjected to fractional extraction, replacing the hexane at predetermined time intervals and determining the viscosity of each extract (temperature of extraction 19–21° C). Table 1 shows the results as obtained

TABLE 1  
SUMMARY OF MOLECULAR WEIGHT DATA ON HEXANE-SOLUBLE FRACTIONS  
OF ACETONE-EXTRACTED *CRYPTOSTEGIA* RUBBER

Fraction no.	Time in hrs. (accum.)	Percentage extract		Average molecular weight
		Batch	Accum.	
1	12	7.323	7.323	$6.87 \times 10^4$
2	24	10.43	17.753	$7.37 \times 10^4$
3	48	13.44	31.193	$7.88 \times 10^4$
4	72	8.339	39.532	$8.28 \times 10^4$
5	96	6.049	45.581	$8.56 \times 10^4$
6	120	3.083	48.664	$8.89 \times 10^4$
7	144	1.844	50.508	$9.27 \times 10^4$
8	168	1.309	51.817	$10.08 \times 10^4$
9	192	0.626	52.443	$13.35 \times 10^4$

Weight of sample taken: 5.0019 g.

- (1) Total acetone extract: 0.3718 g. = 7.434 per cent
  - (2) Total hexane extract: 2.6230 g. = 52.443 per cent
  - (3) Total residue: 2.0071 g. = 40.12 per cent
- TOTAL = 100.00 per cent

for the various fractions. If these data are compared with the data obtained for prime ribbed smoked sheet for the same times of extraction and under the same conditions (Table 2), one finds that *Cryptostegia* apparently contains many chains of short length and that the initial rate of extraction is far greater for *Cryptostegia* than for *Hevea*. After 192 hours' extraction, an identical amount of rubber hydrocarbon was extracted for both. However, at that time the extraction of the smoked sheet was not complete, whereas the extraction of *Cryptostegia* can be considered as having been finished.

*Cryptostegia* contains more hexane-insoluble gel rubber than smoked sheet, but the molecular weight of the *Cryptostegia* fraction was in all cases lower than that of the corresponding *Hevea* fractions. The distribution curve for *Cryptostegia* shows a very pronounced and sharp maximum at a molecular weight of about  $8 \times 10^4$  (Figure 4.) The molecular-size distribution appears to be extraordinarily narrow and uneven.

TABLE 2

SUMMARY OF MOLECULAR WEIGHT DATA ON HEXANE-SOLUBLE FRACTIONS FROM ACETONE-EXTRACTED SMOKED SHEET

Fraction no.	Time in hrs. (accum.)	Percentage extract		Average molecular weight
		Batch	Accum.	
1	6	2.818	2.818	$8.73 \times 10^4$
2	12	2.405	5.223	$11.35 \times 10^4$
3	24	5.186	10.409	$9.14 \times 10^4$
4	36	4.515	14.924	$10.80 \times 10^4$
5	48	4.673	19.597	$10.90 \times 10^4$
6	60	3.865	23.462	$11.06 \times 10^4$
7	72	5.658	29.120	$12.36 \times 10^4$
8	84	3.352	32.472	$12.76 \times 10^4$
9	96	3.175	35.647	$13.42 \times 10^4$

Weight of sample taken: 5.0720 g.

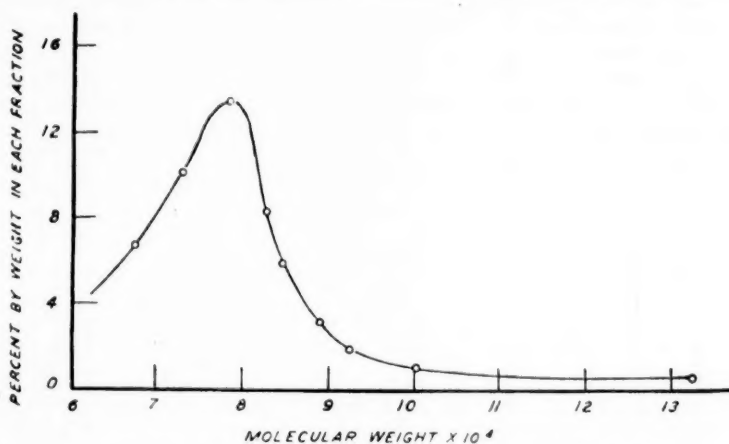
(1) Total acetone extract: 0.1580 g. = 3.12 per cent

(2) Total hexane extract: 2.900 g. = 57.17 per cent

(3) Residue: 2.0140 g. = 39.71 per cent

TOTAL = 100.00 per cent

In general it can be said that *Cryptostegia* consists mainly of two different lengths of molecules, one within the range of about  $8 \times 10^4$ , the other in the hexane-insoluble gel part of the rubber. Only a small proportion of the total rubber has a molecular weight between  $9$  to  $13.5 \times 10^4$ . In this respect *Cryptostegia* must be considered very different from smoked sheet, where we find a more even and uniform distribution of molecular chain length<sup>7</sup>.

Fig. 4.—Distribution Curve of Hexane-Soluble Fractions of *Cryptostegia*

#### FRACTIONATION AND MOLECULAR WEIGHT DETERMINATION OF GUAYULE UNMILLED ACETONE EXTRACTED GUAYULE

To avoid surface oxidation, each sample was taken from the interior of a large block. It was dried in a vacuum desiccator, cut into thin strips, and subjected to acetone extraction at room temperature. 19.4 per cent of resin could thus be removed. Then the sample was again vacuum-dried and sub-

jected to fractionation in hexane after it had been placed in a cotton bag. The extracts were rather muddy, especially those obtained from the first fractionation. Therefore, they were subjected to a quick centrifugation at 5,000 r.p.m. It is well known that stirring has some effect on the molecular weight of the high polymer, and we may expect a similar effect from centrifuging. However, inasmuch as all guayule samples had been subjected to the same treatment, we may at least consider the results in a comparative way.

TABLE 3

SUMMARY OF MOLECULAR WEIGHT DATA ON HEXANE-SOLUBLE FRACTIONS OF ACETONE-EXTRACTED UNMILLED GUAYULE RUBBER

Fraction no.	Time in hrs. (accum.)	Percentage extract		Average molecular weight
		Batch	Accum.	
1	3	9.745	9.745	$8.97 \times 10^4$
2	6	10.63	19.775	$9.34 \times 10^4$
3	12	16.25	36.025	$9.49 \times 10^4$
4	24	14.81	50.835	$9.73 \times 10^4$
5	36	9.37	60.21	$10.18 \times 10^4$
6	48	5.91	66.12	$11.82 \times 10^4$
7	60	1.47	67.59	$16.03 \times 10^4$

Weight of sample taken: 4.2230 g.

(1) Total acetone extract: 0.8188 g. = 19.39 per cent

(2) Total hexane extract: 2.8794 g. = 67.59 per cent

(3) Total residue: 0.4923 g. = 11.62 per cent

TOTAL = 98.60 per cent

The clear solution was then decanted and the residue, apparently consisting mainly of cellulosic matter, was discarded. Complete solution of guayule rubber was obtained in hexane. The viscosity of the clear solutions was determined with an Ostwald viscometer. Table 3 records the fractionation and the average molecular weights calculated therefrom. By the method of differentiation, it was possible to calculate the amount of residue from the amount of resin extracted and the total amount of the hexane extracted ma-

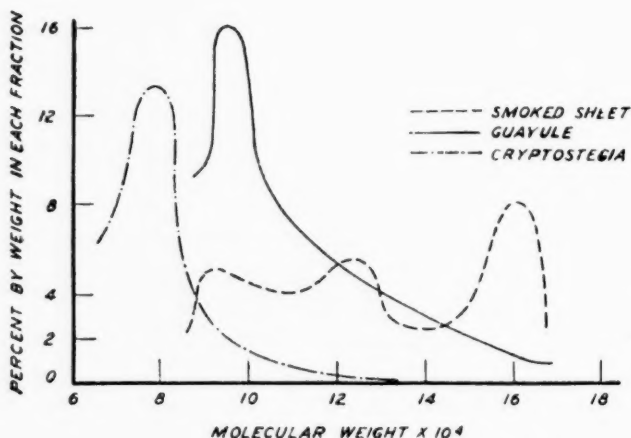


FIG. 5.—Distribution Curve of Hexane-Soluble Fractions of Rubber obtained from Different Plants

terial. However, it is possible that too high a figure was obtained by this method of calculation for the amount of residue. Previous work had indicated that the complete removal of resin from guayule rubber is very difficult, and often not obtainable by the use of acetone as solvent<sup>3</sup>.

In this connection, it should be mentioned that previously reported molecular weights of guayule are higher<sup>8</sup> than those now reported. This is due to the fact that Staudinger's equation always gives higher results than that of Arrhenius.

Figure 5 gives a schematic survey of the relation of molecular weight to percentage solvent extractable rubber to Hevea, *Cryptostegia* and guayule<sup>9</sup>.

#### MILLED ACETONE-EXTRACTED GUAYULE

Since guayule shows a very pronounced and extraordinarily speedy breakdown during milling, it was thought of interest to determine the effect of sheeting on the mill. The sample was passed three times through the cold rolls of a standard laboratory mill (opening 0.04 inch). It was then acetone-extracted and subjected to the same extraction and purification procedures as the unmilled sample. Table 4 shows the molecular weights as calculated from the viscosities of the various fractions<sup>9</sup>.

TABLE 4

SUMMARY OF MOLECULAR WEIGHT DATA ON HEXANE-SOLUBLE FRACTIONS OF MILLED GUAYULE RUBBER

Extraction no.	Time in hrs. (accum.)	Percentage extract		Average molecular weight
		Batch	Accum.	
1	3	3.024	3.024	$6.67 \times 10^4$
2	6	3.205	6.229	$7.75 \times 10^4$
3	9	4.153	10.382	$7.33 \times 10^4$
4	18	13.56	23.942	$7.82 \times 10^4$
5	30	19.14	43.082	$7.72 \times 10^4$
6	44	11.60	54.682	$7.86 \times 10^4$
7	56	5.732	60.414	$7.82 \times 10^4$

Weight of sample taken: 4.2531 g.

(1) Total acetone extract: 0.8045 g. = 18.91 per cent

(2) Total hexane extract: 2.8647 g. = 67.36 per cent

TOTAL = 86.27 per cent

The decrease in the rate of extraction of the milled guayule sample can be explained only by the somewhat changed experimental conditions which had to be applied because of the great tackiness of the milled sheet. To prevent it from sticking together during fractionation, it was rolled into parchment paper and extracted with hexane in this condition. This may account for a somewhat slower diffusion than that of the unmilled sample which was surrounded by a cotton bag only. Total solution again took place and the accumulative percentage extracts of the unmilled and the milled sample check very closely. However, the molecular weight of the various fractions decreased considerably during the sheeting process. The greatest breakdown was found in the higher molecular-weight fractions (approximately 50 per cent). The molecular weight of all the fractions of the milled guayule can—to all intents and purposes—be considered the same.

This indicates the tremendous susceptibility of guayule rubber to breakdown on the mill, and in a great many instances may account for the poor



physical properties of its vulcanizates and the variations in results as previously discussed. Extreme care in compounding seems to be necessary to obtain reasonable results, a condition which, of course, is difficult to maintain during any kind of production. Figure 6 shows a comparison between the milled and unmilled guayule.

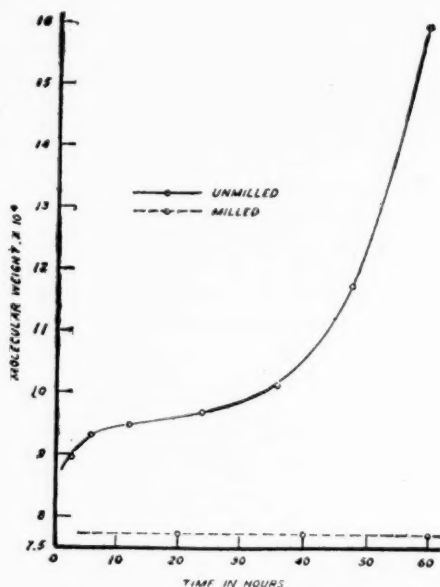


Fig. 6.—Extraction of Hexane-Soluble Fractions of Acetone Extracted Guayule

### MORPHOLOGICAL INVESTIGATIONS

This difference in molecular size and configuration is also clearly demonstrated by studying the preparation microscopically using ultra-illumination with incident light<sup>8</sup>. While *Hevea* shows globules and threads of varying sizes and shapes, *Cryptostegia* exhibits very small spherical globules and extremely fine but uniformly dimensioned threads<sup>10</sup>.

Guayule is also in line with these findings. The soluble fraction forms very large globules<sup>10</sup>, indicating a high percentage of low molecular weight components.

These findings are in full accord with Staudinger's point of view<sup>11</sup> and disprove the opinion expressed by Stamberger and Blow<sup>9</sup> which was based on osmotic pressure measurements.

### SUMMARY

In general it can be said that the molecular-size distribution of *Cryptostegia* as well as guayule rubber is very much different from that of *Hevea*. The length of the *Cryptostegia* chains are within the range of the *Hevea* chains, but their distribution is not as even as those of the latter. Guayule must be considered as a rubber of much lower molecular weight.

1 India  
2 Dolley

3 Haus  
4 Kemp  
5 Haus  
6 Haus

7 Wan  
8 Loud  
9 Stam  
10 Hau  
11 Stau

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# THE VISCOSITY-MOLECULAR WEIGHT RELATION FOR NATURAL RUBBER \*

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## INTRODUCTION

Houwink<sup>1</sup> and Flory<sup>2</sup> have shown that the Staudinger law in its simplest form, relating intrinsic viscosity to molecular weight deduced from thermodynamic properties of the polymer solutions through the equation:

$$[\eta] = KM \quad (1)$$

is not in agreement with experiment.

Both these authors agree that the correct relation is given by:

$$[\eta] = KM^a \quad (2)$$

where in the case of polyvinyl acetate compounds and polymethacrylate  $a \approx 0.6$  (Houwink) and in the case of polybutene  $a = 0.64$  (Flory). More recently Mark and Bartovics<sup>3</sup> found that  $a$  varies from 0.7 to 1.0 for polystyrene prepared at different temperatures in toluene and  $a = 0.67$  for cellulose acetate in acetone. However, it seemed to us very important to check the validity of relations (1) or (2) on the very material for which Staudinger deduced his relation, i.e., polyisoprene, (natural rubber), since in this case no argument of the type generally put forward by Staudinger and his coworkers can be made that the deviations from Equation 1 are due to the specific character of the polymer structure.

## EXPERIMENTAL

**Molecular Weight Determination. Osmometer.**—The molecular weight was determined from osmotic pressure measurements, using a cell identical with that described by Flory<sup>4</sup>, so no further description of it is necessary.

**Membrane.**—It was found, however, that the membranes described by Flory required long and slow measurements and became less and less permeable with time; this is probably due to the difference in solvents used—benzene and cyclohexane in the case of Flory, toluene in our case. It definitely appears that in toluene these denitrated colodion membranes are slowly dehydrated. Following a suggestion of R. M. Fuoss<sup>5</sup>, we have used collodion membranes without denitration. These membranes proved extremely satisfactory for polymers of molecular weight above 30–40,000 and for hydrocarbon solvents. They allow fairly rapid measurements, about 1 to 1.5 hours per solution, and the same membrane, if kept continuously in contact with toluene, can be used over a very long period of time. As a matter of fact, we are still using one of our membranes after twelve months of service. Since this type of membrane proved so

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successful, it seems useful to include the details of its preparation, although it is similar to the one given by Fuoss and Mead<sup>6</sup>. Twenty cc. of solution containing 72% c.p. Merck collodion, 14% ether, and 14% ethyl alcohol are poured into an iron ring, about 10 cm. in diameter, floating on a mercury surface and allowed to dry under a slow current of air. As soon as feasible (prolonged drying decreases the permeability) the film is transferred to water, which precipitates the collodion and removes the solvent. The iron ring is disengaged, the membrane stands in water overnight, then is placed successively in water-alcohol, alcohol, alcohol-toluene, and toluene in each case, for two hours. Before the membrane is used, however, it is necessary to age it by letting it stand for about a week in pure toluene. This precaution is necessary because an unaged membrane was found to give erratic and irreproducible results.

*Temperature.*—The osmometer was placed in a large thermostat with extremely powerful agitation, controlled within  $\pm 0.1^\circ$ . A better temperature control proved unnecessary, provided the temperature was uniform and the temperature variation in the course of a measurement (1 hour) did not exceed  $\pm 0.05^\circ$ .

*Method of Measurement.*—The method used is a combination of the dynamic and static method. Equilibrium is approached first from one side; as soon as equilibrium is neared the adjustment is changed and equilibrium is approached from the other side. Measurements are made every few minutes and, if necessary, the data can be plotted. In general the precision of each equilibrium value is about 3–5 per cent. As soon as the measurement is finished, the solution side of the osmometer is rinsed with toluene and filled with pure solvent. Readings are taken to determine any adsorption by or inhomogeneities in the membrane. The resulting corrections were, without exception, virtually negligible.

*Extrapolation to  $(\pi/c)_{c=0}$ .*—Each fraction was measured at several different concentrations, three of them at as many as seven concentrations and  $\pi/c$  was then plotted against  $c$  for these three fractions. This relation proved to be linear in the range of concentrations used, as is to be expected on the basis of theories of Flory<sup>7</sup> and Huggins<sup>8</sup>. No correction for the difference in density between solvent and solution was applied, since control measurements have shown this correction to be almost negligible for the concentrations used, and the curves extrapolate to the same value of  $(\pi/c)_{c=0}$  in any case. In the case of the subsequent fractions the slope of  $\pi/c$  vs.  $c$  was considered identical with the one found above. No discrepancies were found.

*Concentration Determination.*—The concentration was always determined by high vacuum evaporation of a known amount of the undiluted solution. The determinations were accurate to 1–2 per cent. All concentrations have been expressed in grams of rubber per 100 cc. of solvent.

*Viscosity Determination.*—The viscosity was determined on a carefully calibrated and systematically checked Ostwald viscometer with the usual technique. It was found experimentally, that, provided  $\eta_{rel.}$ , the relative viscosity of the solution, was below 1.3, the intrinsic viscosity was independent of the concentration. Repeated checking has shown that the values of the intrinsic viscosity  $[\eta]$  determined on solutions of different concentrations agreed to 2–3 per cent. All the viscosities have been determined at  $25^\circ$ .

*Material.*—The Hevea used in this experiment was ribbed smoked sheet<sup>9</sup>. The toluene was the commercial solvent, dried with calcium chloride.

*Fractionation.*—The extraction and fractionation of Hevea proved to be a

delicate problem if the oxidative degradation of the high molecular weight fractions was to be avoided and at the same time a narrow fractionation obtained. After repeated failures it was found necessary to extract the soluble fraction in a refrigerator, below  $0^{\circ}$  under carbon dioxide. All the fractions had to be kept in darkness, in presence of an antioxidant and carbon dioxide.

The fractionation method was fractional precipitation by methyl alcohol from toluene solutions. A few of the fractions proved to be fairly large and had to be refractionated, but usually the primary fractions were small enough, thus avoiding the necessity of refractionation, a process which always involves the danger of degradation.

Experiments were made on fractions from three different fractionation series; the results lie close together.

### RESULTS

The results of the measurement of twenty-two different fractions ranging from 40,000 to 1,500,000 are presented in Figure 1. The points marked with a question mark correspond to fractions where the possibility of a slight permeability of the membrane cannot be excluded.

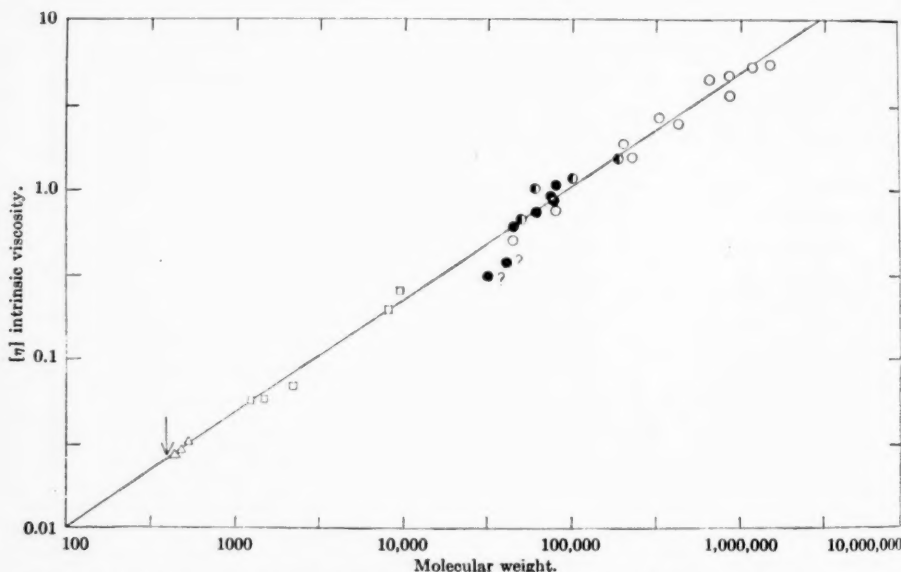


FIG. 1.—Viscosity-molecular weight relation for Hevea rubber: Carter and Magat, ○ Fractionation 1, ● Fractionation 2, ● Fractionation 3 (? indicates evidence of possible permeability of the membrane); □ Kemp and Peters; Δ Staudinger and Staiger.

As one can see, the results are represented accurately by an expression of the form of Equation 2, where  $K = 5.0 \times 10^4$  and  $W = \frac{2}{3}$ .

To extend our  $[\eta]$  vs.  $M$  relation toward lower molecular weights, we have used the data of Kemp and Peters<sup>10</sup> on degraded rubber, in which they have determined the viscosity and the freezing point lowering of several polyisoprene fractions. An extension of the Flory-Huggins theory of thermodynamical properties of rubber solutions shows that the freezing point lowering

$\Delta T_f$  of rubber solutions depends on the concentration according to:

$$\left( \frac{\Delta T_f}{c} \right)_{c=0} = \left( \frac{\Delta T_f}{c} \right) - bc \quad (3)$$

This linear dependence of  $\Delta T_f/c$  on concentration was found experimentally by Kemp and Peters. We have used this relation to extrapolate their freezing point lowering data to  $c = 0$  and so to obtain the true thermodynamic molecular weights of their fractions. Although it cannot be expected *a priori* that the constants  $K$  and  $a$  should be exactly the same for toluene and benzene, it was actually found that the points of Kemp and Peters corresponding to molecular weights between 1,000 and 9,000 fall, within the limits of error, on our line extrapolated from the high molecular weight range<sup>11</sup>.

In much the same way the viscosities of pure hydrocarbon (hentriacontane, ethylene, triacontane and ethylidene triacontane) solutions in benzene as determined by Staudinger and Staiger<sup>12</sup> fall exactly on our curve.

It can, therefore, be stated that the relation derived above is valid for molecular weights ranging from 420 to 1,500,000, and there is no reason to suppose that any change should occur for even higher molecular weights. On the contrary, an extension toward lower molecular weights seems dubious, since it is to be expected that the mechanism of viscosity changes for short hydrocarbon chains.

If the constants  $K$  and  $a$  are now revised in order to fit best *all* the data, we find:

$$[\eta] = 5.02 \times 10^{-4} M^{0.667} \quad (4)$$

The limits of error for  $K$  are  $4.98 < K < 5.02$  and for  $a$ :  $0.660 < a < 0.673$ .

## DISCUSSION

*Data of Previous Authors.*—It is to be expected that, for unfractionated or only roughly fractionated samples, the number average molecular weight as determined from thermodynamic data will be much lower than the weight average molecular weight determined from the viscosity (see also following paragraph). It is, hence, to be expected that the points determined by various authors who did not go through the elaborate procedure of careful fractionation will lie above our curve. This deviation is to be expected to be larger the broader the fractions are, and particularly so for the high molecular-weight, difficulty soluble, fractions. The generally narrower, lower molecular-weight fractions are expected to lie closer to our curve. That this prediction is realized can be seen from Figure 2, which includes data of Gee<sup>13</sup>, Meyer and Wertheim<sup>14</sup>, and Staudinger and Fisher<sup>15</sup>.

*Viscosity Average Molecular Weight.*—It was pointed out by Lansing and Kraemer<sup>16</sup> that the molecular weight determined from the viscosity with help of the Staudinger relation is equal to the weight average molecular  $\bar{M}_w$ :

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} \quad (5)$$

This is no longer exactly true if the Staudinger relation (Equation 1) is replaced by the more general Equation 2.

In this case we have to go back to the definition of the average weight. For a relation of the type of Equation 2 the average weight  $\bar{M}_v$  is given by definition as:

$$\bar{M}_v = \left( \frac{\sum n_i M_i^{a+1}}{\sum n_i M_i^a} \right)^{1/a} \quad (6)$$



If  $a$  is of the order of  $\frac{1}{3}$ , as seems to be the case for most of the polymers so far investigated,  $\bar{M}_v$  is still far closer to  $\bar{M}_w$  ( $a = 1$ ) than to  $\bar{M}_n$  ( $a = -1$ ), although it is no longer identical with it.

**Theories of Viscosities of Chain Polymers.**—No theory of the viscosity-molecular weight relation of elastomer solutions presented so far represents exactly the observed features. The following remarks, although they do not give a theory, may be of use as a lead for the development of one.

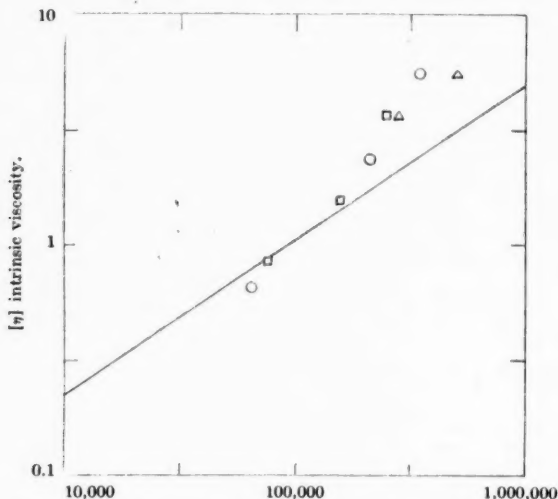


Fig. 2.—Results of previous investigators on poorly fractionated material:  $\circ$  Gee;  $\square$  Staudinger and Fischer;  $\Delta$  Meyer and Wertheim.

Some years ago Kuhn<sup>17</sup> pointed out that the flow of coiled molecules in solution must follow one of the two following patterns:

**Mechanism I.**—The polymeric molecule and the solvent entrapped, "immobilized", between its segments move together, forming a sphere (or an ellipsoid) to which Einstein's hydrodynamic theory (or its extensions) can be applied.

**Mechanism II.**—At least a part of the liquid is free and flows between the segments as through the holes of a mesh. In this case the flowing liquid exerts a torque on each individual segment (or a group of such), as in the case of dumb-bell molecules. In this case the viscosity mechanism is quite different, and the energy lost can be calculated assuming that the sum of the torques has to be zero to avoid an infinitely accelerated rotation of the molecule.

Which one of the two mechanisms predominates depends largely on the degree of separation of segments, that is, on the degree of swelling, the one dissipating the less energy being predominant. It is hard to predict whether the transition from one mechanism to the other is abrupt or continuous, but it can be safely stated that a mechanism of the first type is to be expected in the case of solutions in poor swelling agents, a mechanism of the second type—if it ever exists in the pure form—in good swelling agents. Kuhn<sup>18</sup> has developed mathematical expressions for the viscosities for both mechanisms, but more rigorous demonstrations have been given by Hulburt, Harmon, Tobolsky and Eyring<sup>19</sup> for mechanism I, and by Huggins<sup>20</sup> for mechanism II.

Assuming randomly kinked molecules and applying the formula given by

Daniels<sup>21</sup> for the volume occupied by such a molecule, Hulburt, Harmon, Tobolsky and Eyring<sup>19</sup> found a relation for mechanism I:

$$[\eta] = KM^{\frac{1}{2}} \quad (7)$$

while Huggins found for the second mechanism a relation identical with that of Staudinger:

$$[\eta] = KM \quad (8)$$

As shown in preceding paragraphs, the experimental results for most rubber-like polymers lead to an expression:

$$[\eta] = KM^{0.6-0.7} \quad (9)$$

a power situated between the two values 0.5 and 1 derived theoretically. Two explanations can be advanced for this discrepancy: either in the solvents used we are just in the transition region from one mechanism to the other, or the assumptions concerning the "randomly kinked" shape of the molecule are to be modified. In this connection it ought perhaps to be recalled that, previous to Kuhn, Haller<sup>22</sup> has considered the mechanism II assuming that the rubber molecule is not "randomly kinked" but distributed with a uniform density in all the volume occupied, and obtained a relation:

$$[\eta] = KM^{\frac{1}{2}} \quad (10)$$

which is exactly correct for Hevea and in close agreement with the experiments for other polymers.

### SUMMARY

The osmotic molecular weight-intrinsic viscosity relation for Hevea rubber has been determined and found to correspond to the relation:  $[\eta] = 5.02 \times 10^{-4} M^{0.667}$ .

### ACKNOWLEDGMENT

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# EFFECT OF POLYMOLECULARITY ON DEFORMATION OF BUTYL POLYMERS \*

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Most high polymers exist in a polymolecular state of varying degree, which depends on variations of conditions, modifications, and courses of reaction during polymerization and chain termination<sup>1</sup>. The extent of heterogeneity of molecular weight profoundly affects the deformation behavior of high polymeric substances, as noted in the case of unvulcanized Butyl polymers during a study of their elastic-plastic properties<sup>2</sup>. Differences in physical properties of cellulose derivatives attributable to polymolecularity were recently reported<sup>3</sup>, and improvements in some Buna-S processing qualities were predicted if narrower distributions of molecular weight could be obtained<sup>4</sup>.

Previous study of the processing behavior of elastomers indicated the desirability of investigating the effects of carefully controlled molecular weight and molecular weight distribution on the deformation characteristics of the material. Butyl rubber lends itself well to the study of individual molecular species and combinations of them because of several properties. (1) Butyl rubber is essentially a long-chain polymer with no detectable branching<sup>5</sup> or cross-linking. For this reason it is completely soluble (that is, free of gel polymer); this solubility facilitates a fractionation procedure by solution and subsequent precipitation of all molecular weight species. (2) Butyl rubber is not readily changed by short term storage at room temperature and, in the case of normal molecular weights, manipulations such as slight milling and molding result in little change in molecular weight.

It is realized that various types of elastomeric molecules differ in extent of branching, amount and type of substituted side groups, unsaturation, and degree of chain kinking. However, it is believed that differences in deformation behavior attributable to molecular-weight distribution as measured for one polymer should have some interrelation with other types. Therefore, the effect of variations in molecular weight and of molecular weight distribution on the properties of Butyl should be of universal interest in connection with the subject of rubberlike behavior.

## SAMPLE PREPARATION

In general the fractionation procedure was similar to that evolved by Flory for polyisobutylenes<sup>6</sup>. One hundred-gram portions of a Butyl rubber were dissolved in 10,000 cc. of dried benzene and the precipitation was carried out with dried acetone at 25° C in a constant temperature water bath. Eight 100-gram portions were fractionated into nine relatively narrow molecular weight cuts; the respective cuts were then combined by solution in naphtha, reprecipitated, and dried in vacuo at 80° C. The fractionation was so designed

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that the middle or fifth fraction of the nine obtained would be a central building block for blends of greater molecular-weight distribution with constant average molecular weight.

*Individual Fractions and Molecular Weights.*—Table I lists the fractions obtained and their respective viscosity-average molecular weights<sup>6</sup>, obtained from intrinsic viscosities in diisobutylene. An estimated limit for the fraction is placed between each molecular weight value for the various fractions. An initial threshold molecular weight value (an upper limit for fraction 1) was determined on a similar sample of Butyl polymer by another member of these laboratories.<sup>7</sup> In estimating limits between fractions, it is fully realized that such values are only idealistic in nature since, in any fractionation process, a certain amount of overlapping of the molecular species between two adjacent cuts always exists<sup>8</sup>. The degree of overlapping is largely dependent on the dilution of the polymer in the solvent before fractionation.<sup>9</sup>

TABLE I  
COMPOSITE OF FRACTIONS FROM ORIGINAL BUTYL

Fraction	Composite of fractions from eight 100-gram portions of original Butyl					Check fractionation composite of fractions from two 100-gram portions of original Butyl				
	Cc. acetone per 100 cc. benzene	Weight (%)	Intrinsic viscosity	Viscosity-av. mol. wt.	Estd. limit between fractions	Cc. acetone per 100 cc. benzene	Weight (%)	Intrinsic viscosity	Viscosity-av. mol. wt.	
					1,000,000					
1	0-4	8.0	1.592	545,000	515,000	0-4.0	13.0	1.648	570,000	
2	4-4.5	16.2	1.518	500,000	480,000	4.0-4.5	17.7	1.503	500,000	
3	4.5-5.0	14.0	1.381	440,000	400,000	4.5-5.0	14.6	1.330	420,000	
4	5.0-5.5	13.0	1.249	375,000	330,000	5.0-5.0	9.0	1.152	340,000	
5	5.5-6.0	9.0	1.089	295,000	260,000	5.5-6.0	7.5	1.026	280,000	
6	6.0-7.0	8.4	0.935	236,000	220,000	6.0-7.0	10.4	0.944	240,000	
7	7.0-8.0	7.6	0.853	206,000	170,000	7.0-8.0	7.3	0.798	190,000	
8	8.0-10.0	8.4	0.648	134,000	85,000	8.0-10.0	6.4	0.658	136,000	
9	10.0+	12.0	0.344	50,000	20,000	10.0+	12.0	0.373	56,000	
Total recovered		96.6					97.9			

To check the reproducibility of the fractionating procedure and the molecular-weight determinations, a second series of fractionations were run. In the second check fractionation, two 100-gram portions were precipitated into the same nine components as in the previous experiment. Their molecular weights are listed in the right-hand columns of Table I. Fraction for fraction, comparable viscosity-average molecular weights were obtained. This justifies confidence in the fractionation procedure and subsequent combination of the respective fractions from the original eight 100-gram portions.

*Blends of Increasing Molecular Weight Distribution with Constant Average Molecular Weight.*—The fractionation was designed to obtain a middle fraction from nine cuts as a building stone around which blends of increasing distribution would be based. This is shown schematically in Figure 1, where fraction 5 (Table I) stands as a central component of the variety of blends representing increasing molecular weight distribution. Each fraction (numbered as in Table I) used as a component of the various blends is depicted by a rectangle defined by the weight percentage in the blend and by its ideal molecular weight

limits. The four blends of increasing molecular-weight distribution were made up by dissolving the various fractions in naphtha, concentrating these solutions on a water bath, and precipitating the blend with acetone and methyl alcohol. Drying in a vacuum oven at 80° C completed the operation.

Blend 1 is fraction 5, and its originally determined molecular weight of 295,000 is similar to the average molecular weights of blends 2, 3, and 4. With blend 4 the fractional components were recombined in the same proportions in which they were originally precipitated. Below the original experimental molecular weight of blend 1, Figure 1, gives a redetermined molecular weight after this fraction had been sheeted on a mill and molded for plasticity determinations. Only a slight decrease in molecular weight was noted, and this was within experimental error of the determinations. After blends 2, 3, and 4 had been formed by the solution method, experimental molecular weights were

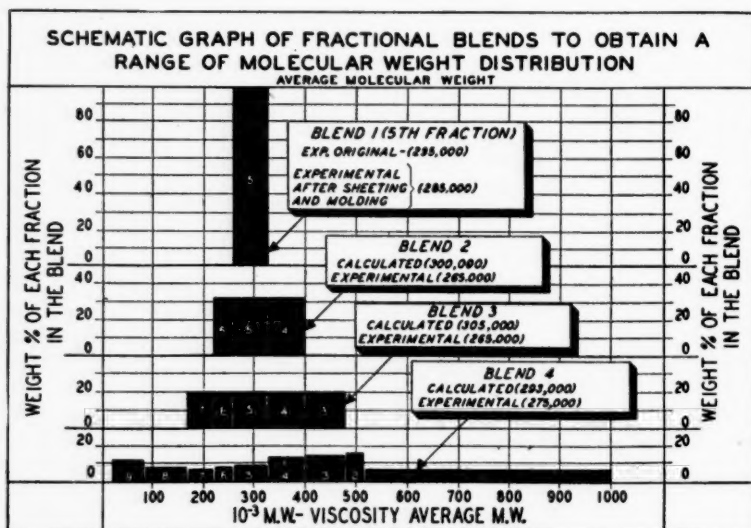


FIG. 1

compared with those obtained by calculating an arithmetic average of the component intrinsic viscosities. (These experimental values were determined after the blends had been sheeted and molded for plasticity tests.) Although the experimental values are a little lower than the arithmetic averages, all blends show similar experimental molecular weights. Comparisons are made in Figure 1.

#### EFFECT OF MOLECULAR WEIGHT VARIATIONS UNDER CONSTANT DEFORMATION RATE

A large variety of operations for the processing of rubberlike substances deform the material under conditions of constant deformation at a given rate—for example, mixing mills, calenders, and generally tubers operate at a predetermined speed, regardless of the original consistency of the polymer. The resistance to deformation offered by the particular polymer or compound is manifested in the power requirements for the operation.

In a previous publication from this laboratory<sup>2</sup> it was recognized that measuring plasticity and elasticity of elastomers under some condition of constant rate of deformation would be helpful in predicting the processing behavior of a variety of polymers. By this method certain elastic-plastic properties of Butyl were correlated with extrusion swell and, later, with mill behavior. The arbitrary conditions of constant deformation were established and essentially consisted of determining the load or force required to compress a molded cylindrical pellet 50 per cent of its original height in 10 seconds. After the compression the elastic recovery in 15 seconds was followed by a dial gage. The measurements were made over a range of temperatures and yielded information on the thermoplastic and thermoelastic characteristics of the polymers in question. Early in the initial studies it was noted that large variations in molecular weight distribution were accompanied by large differences in thermoplasticity and thermoelasticity. In the ensuing discussion the initial observations are confirmed by the more refined blending of narrow molecular weight fractions.

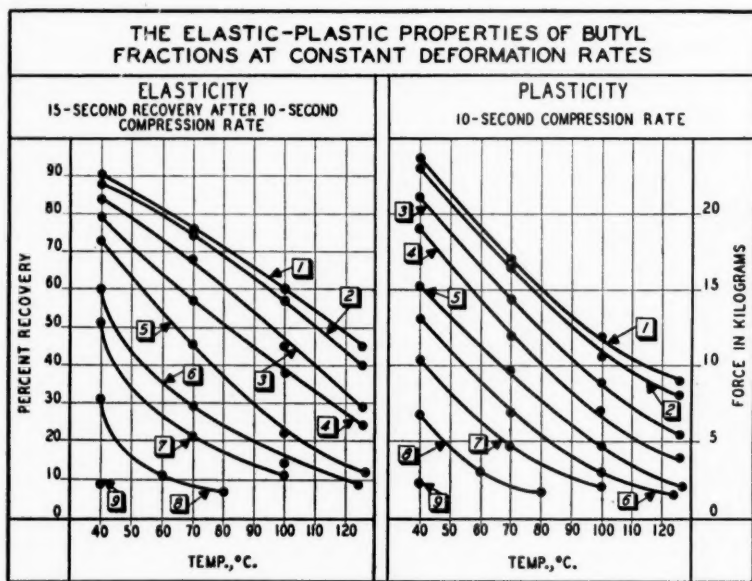


FIG. 2

**Elasticity and Plasticity.**—Figure 2 shows the thermoplastic and thermoelastic behavior of the various uncompounded narrow fractions of Table I, characterized by the constant deformation rate test just described. On the right-hand side of Figure 2 the plasticity-temperature relations show that temperature increases induce sharp decreases in the force or work required to compress the polymer. The positions of the separate curves drop progressively on the chart, with little change in slope as the molecular weight of the fraction decreases. The numbers on each curve refer to the fractions listed in Table I. Plasticity is shown as the load in kilograms required to compress the polymer at the 10-second rate.



Elasticity, measured as percentage recovery in 15 seconds after the 10-second compression, decreases sharply with temperature increase. The positions of the separate curves again drop progressively as molecular weight decreases but, over the temperature range defined, there is a trend toward steeper slopes in the region between 40° and 80° C. For fraction 1 to have an elasticity of 15 per cent, for example (as does fraction 5 at 127° C), the temperature would have to be in the neighborhood of 180° C, according to visual extrapolation. Thus it would be possible to process linear polymers of high molecular weight that are capable of vulcanization, if the problem of premature vulcanization at this temperature of 180° C (scorch, in rubber processing terminology) could be eliminated. Since such a limitation is still present with the usual accelerators of vulcanization, in addition to the inconvenience of extremely high temperature-forming operations, practicality dictates the use of polymers of lower molecular weight.

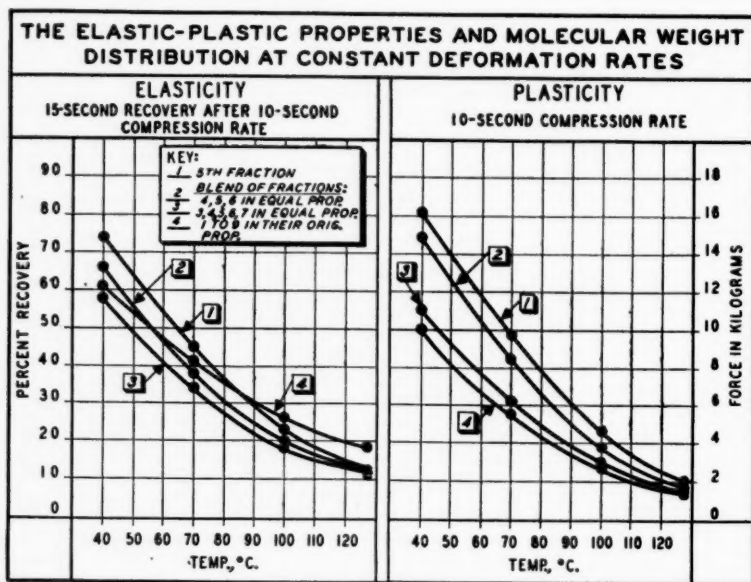


FIG. 3

*Molecular Weight Distribution and Elastic-Plastic Behavior.*—Blends of varying molecular-weight distribution with constant average molecular weight, as defined in Figure 1, were studied by the constant-deformation-rate plasticity method over a temperature range of 40° to 127° C. Although average molecular weights are essentially the same, Figure 3 shows that the blends exhibit different thermoplastic and thermoelastic properties. Blend 1 has the narrowest range of molecular-weight distribution and is the most thermoplastic (plasticity curve 1, Figure 3). As molecular-weight distribution is increased with blends 2, 3, and 4, the mixtures become less thermoplastic. At room temperature or 40° C the narrower distributions are more resistant to deformation as measured by the required work of compression; but at high temperatures, because of differences in thermoplasticity, the force requirements become essentially identical.

In thermoelastic behavior somewhat similar parallels are noted (Figure 3). Elasticity curve 1 represents the narrowest distribution and exhibits the greatest decrease in recovery as temperature approaches 127° F. Curves 2 and 3 show decreasing average slopes as molecular-weight distribution is increased. The recovery values for molecular mixtures 1, 2, and 3, which are spread at 40° C, converge toward a common value at higher temperatures. In blend 4 the effects of extremes in molecular weight species are graphically portrayed. Such a molecular mixture not only has less change in recovery or elasticity with temperature, but its behavior is such that its temperature recovery curve crosses the other varieties, so at 127° C it has a higher recovery value than the others. This effect of molecular extremes in the thermoelastic properties of raw Butyl polymer was evident in earlier work. Thus such a polymer should yield an inferior extruding material from the standpoint of swell. It appears, therefore, that a higher molecular weight could be tolerated in a polymer where the distribution of molecular species is held within narrow limits.

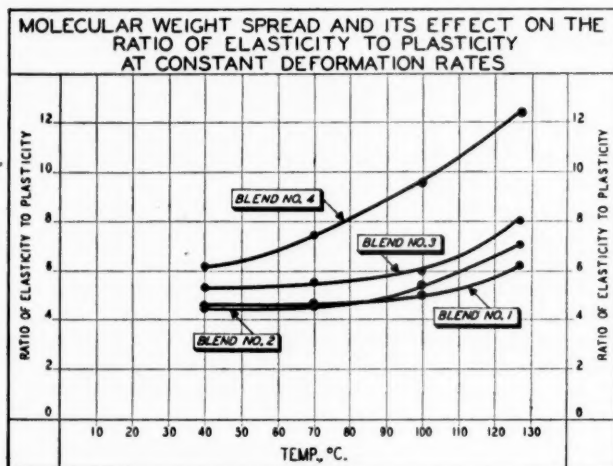


FIG. 4

**Processing Implications.**—If the ratio of elasticity (measured as percentage recovery) to plasticity (measured in kilograms) is determined at various temperatures from the respective curves of Figure 3, an indication of a change in the relation of elasticity to plasticity with variation in temperature is readily obtained. In Figure 4 this change in the relation of the two properties is shown as a function of temperature for the four degrees of molecular-weight distribution. Figure 3 shows that, individually, both elasticity and resistance to deformation decrease with increase in temperature; however, the curves of Figure 4 indicate that, in relation to plasticity, elasticity has a tendency to increase.

The behavior of these polymers is manifest in part by their tendency to lace during a mill mixing operation. The data of Figure 5 show this relation. As the ratio of elasticity to plasticity increases, the temperature at which lacing occurs decreases. A partial explanation of this phenomenon lies in the fact that, as temperature is increased, both film strength and elasticity decrease.

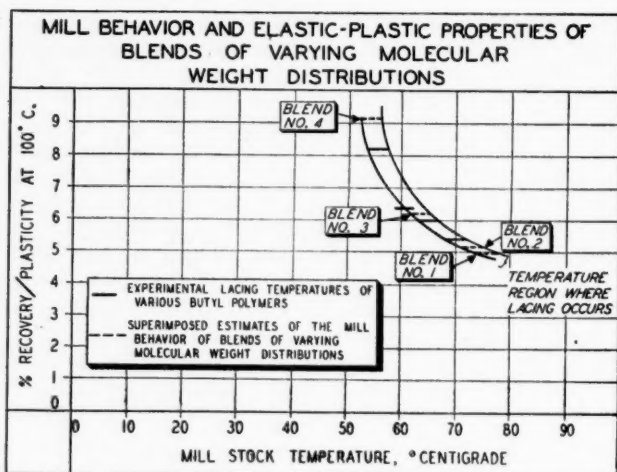


FIG. 5

However, if elasticity does not decrease at a similar or greater rate, the elastic tension present will be sufficiently strong to produce breaks in the polymer band after it has traveled through the roll nip.

Another manifestation of elasticity, plasticity, and their ratios at various temperatures is noted in extrusion behavior. When an elastomer is forced through an orifice under pressure, its elastic component of deformation at that rate governs the degree of swelling after it emerges from the aperture. More specifically, it was shown<sup>2</sup> that swelling after an extrusion operation is directly related to the ratio of elasticity to plasticity of the particular Butyl polymer in the range of extrusion temperatures (100° to 130° C). Theoretically no swelling would occur after extrusion if there were no elastic component of deforma-

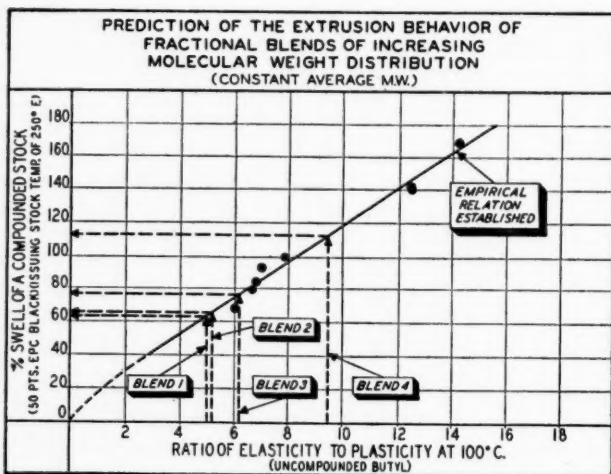


FIG. 6

tion; in this case the ratio under discussion would be zero. Therefore, blend 4 (Figure 4) would exhibit the highest degree of swelling after an extrusion operation, with the others showing descending degrees based upon their elasticity-plasticity ratios in the region of 100° to 130° C.

An obvious question arises concerning the effect of compounding ingredients (notably fillers) on the relative performance characteristics of these polymers. Actually the extrusion data referred to previously were obtained on loaded compounds (50 parts of EPC black), and the indicated performance was related to the ratios of elasticity to plasticity as obtained on the raw polymer. To illustrate this point, Figure 6 reproduces the pertinent data from Zapp and Gessler<sup>2</sup> which established this relation. The behaviors of the polymer blends under investigation are predicted from their elasticity-plasticity ratios. A variation in the amount and type of filler would change the actual performance of the compounds, but the differences among them would remain the same on a relative basis.

#### EFFECT OF MOLECULAR WEIGHT VARIATIONS UNDER CONSTANT LOAD DEFORMATION

In addition to processing concepts involving constant deformation rates, other operations involving considerations of deformation under constant load are sometimes encountered in fabricating articles from elastomers. Machine butt-splicing operations in inner-tube manufacture, for example, frequently utilize clamps which subject the unvulcanized article to a constant load deformation. Permanent injury to this article may result if the elastomer shows too great an irreversible deformation or viscous flow while the operation is being performed.

The literature is profuse with methods of measuring plasticity, elasticity, and deformation characteristics of rubberlike polymers in general, together with empirical equations approximating the observed behavior under various testing conditions. Probably the best and simplest representation of the observed phenomenon is as follows<sup>10</sup>:

$$D_{\text{total}}^{(S,t,T)} = D_{OE} + D_{HE} + D_{\text{visc}} \quad (1)$$

where  $D_{\text{total}}$  = total deformation

$D_{OE}$  = ordinary elastic deformation (mechanically reversible)

$D_{HE}$  = high elastic deformation (mechanically reversible)

$D_{\text{visc}}$  = viscous deformation (mechanically irreversible)

This general equation was supplied with an expression for  $D_{HE}$  by Alexandrov and Lazurkin<sup>11</sup>:

$$D_{\text{total}} = \frac{S}{E_{OE}} + \left( \frac{S}{E_{HE}^\infty} \right) [1 - e^{(-t/\tau)}] + \frac{St}{\eta} \quad (2)$$

where  $S$  = applied stress

$E_{OE}, E_{HE}^\infty$  = Young's moduli (ordinary and high elastic moduli)

$\tau$  = orientation time

$\eta$  = internal viscosity

$t$  = time

$D_{OE} = S/E_{OE}$ , where  $E_{OE}$  is of a relatively high order of magnitude and the stress,  $S$ , is generally low for the usual run of laboratory tests; therefore  $D_{OE}$  may be neglected and leaves but two components to be isolated.

To study deformation under constant load and thereby separate these two components, a Williams parallel-plate plastometer was modified and placed in a constant temperature ( $40^\circ \pm 0.5^\circ \text{C}$ ) circulating-air oven. The modification consisted of reducing the load from 5 to 1.8 kg. One of the most important conditions required in the application of these equations is that the stress per unit area remain constant during the compression cycle. This can be accomplished only if the area in contact with the platens of the plastometer remains constant. Such a condition is realized by applying a restrictive surface of fine sandpaper to the faces of the platens and prohibiting compression under the free load from exceeding 38 to 40 per cent of the original height of the cylindrical pellet. (Pellet dimensions are 0.5 inch high and 0.75 inch in diameter.) With these precautions no lateral flow takes place around the area in contact with the platens, and the pellet is deformed only by bulging at the sides.

If a series of pellets of standard dimensions are compressed to various degrees of deformation by a progressive increase in time of compression, a total deformation curve, such as that of Figure 7, is generated with time. If this

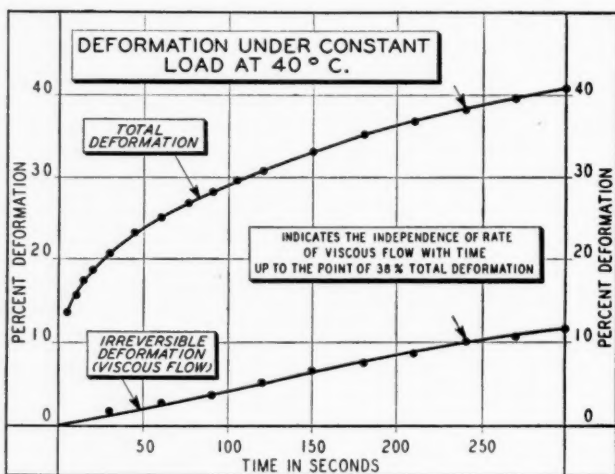


FIG. 7

same series of pellets, which were subjected to the various degrees of compression, are allowed to relax or recover while supported in boiling water, the difference between the original height and the height of the pellet after complete recovery is a measure of viscous flow or irreversible deformation. This series of points is presented in the lower curve of Figure 7. Viscous deformation is linear with time up to the point where total deformation exceeds 38 per cent; at this point the dimensional area of the pellet in contact with the plastometer platens begins to increase. The differences between the ordinate values of curves  $D_{\text{total}}$  and  $D_{\text{visc}}$  generate the progress of the high elastic deformation component with time. As predicted by the expression for high elastic deformation ( $D_{\text{HE}}$  in Equation 2), this component varies exponentially with time and approaches a static or limiting value. After this time has been reached under the conditions of the test, all further deformation is of the viscous or irreversible variety.

**Deformation and Flow of Narrow Fractions.**—Figure 7 shows that, as long as total deformation is kept below 38 per cent, the viscous flow-time relation is linear. Therefore, total deformation under the 1.8-kg. load can be followed as a function of time with a single pellet if the test is terminated below 38 per cent deflection. This compressed pellet can then be allowed to recover in hot water and the height remeasured to obtain a value for viscous flow. A straight line can be drawn through the origin to the final point obtained for irreversible deformation to indicate the progress of viscous flow with time. The slope of this line represents the rate of flow. Check runs can readily be made with only two or three pellets to determine the elasto-viscous properties of a certain polymer sample under the established conditions of constant load deformation.

The first eight fractions of Figure 1 (in this test fraction 9 was too soft for significant readings) were subjected to deformation under the constant load conditions defined; the data are shown in Figure 10. The graph or series of

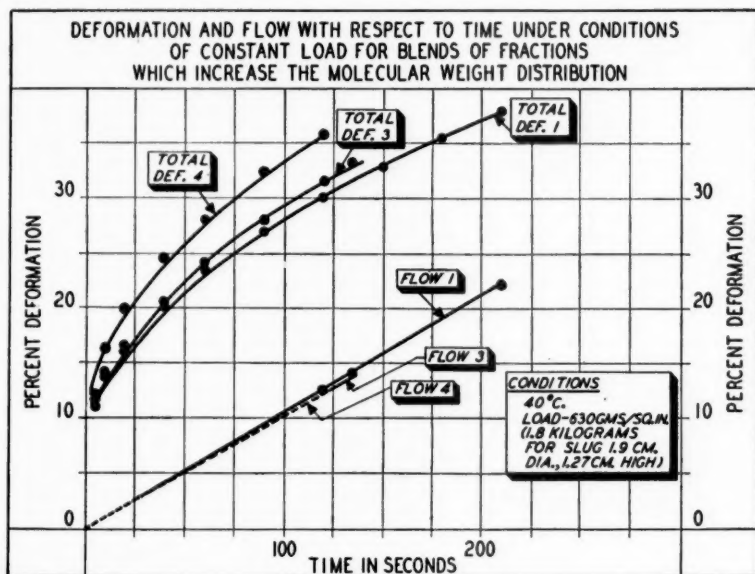


FIG. 8

curves consist of two parts; the solid curved line represents total deformation with time under a load of 630 grams per square cm. at 40° C, and the straight dotted lines represent that portion of the deformation which is irreversible. Thus, the slope of the dotted line would represent the rate of flow, and the difference between the total deformation curve and the flow curve at a given time interval would be a measure of the elastic component of deformation. As the molecular weight of each species is decreased, large differences in rate of deformation and rate of flow are noted.

**Deformation and Flow with Varying Molecular-Weight Distribution.**—The polymers of constant average molecular weight, made up of various distributions of molecular species, exhibit significantly different deformation behaviors under constant load. Total deformation under the conditions shown in Figure 8 is represented by the upper series of curves, and viscous deformation



with respect to time is given by the lower series of straight lines. Because there was a need to conserve fractions for other work, blend 2 was eliminated from this series of experiments. The two sets of deformation curves indicate that, as molecular-weight distribution is broadened (for a given average molecular-weight), a greater total deformation for the same rate of flow is obtained. In other words, a softer but more elastic substance results as molecular-weight distribution becomes wider.

In the sections devoted to constant rate of deformation, it was indicated that the narrow molecular weight distribution was the more processable polymer for a given average molecular weight. Constant load concepts reveal that this advantage is realized with an increase in high elastic modulus of the polymer. In Figure 8 the various molecular weight distributions develop more total deformation as the distribution is increased. Since the flow is the same, increases in the heterogeneity of molecular weight must be accompanied by an increase in elastic deformation. If the sensation of stiffness is defined as time rate of development of high elastic deformation by application of a fixed load, then the polymer blends of widening molecular weight distribution exhibit a progressive decrease in sensation of stiffness—that is, their high elastic moduli is less. From inspection of Alexandrov and Lazurkin's expression for the development of high elastic deformation as an exponential function of time:

$$D_{HE} = \left( \frac{S}{E_{HE}} \right) [1 - e^{-(t/\tau)}] \quad (3)$$

a plot of high elastic deformation against logarithm of time is suggested. However, Rehner<sup>12</sup> shows mathematically, by operating on Equation 3, that high elastic deformation under constant applied stress is directly related to the logarithm of time, provided the proper time limitations are chosen. His equation takes the form:

$$D_{HE} = \frac{-2S}{E_{HE}} \ln t + \text{constant} \quad (4)$$

where the symbols have the same definitions as those of Equation 2. From Equation 4 the slope of the plot of elastic deformation and logarithm of time would be inversely proportional to the high elastic modulus. Such relations are shown in Figure 9.

High elastic deformation, shown as the ordinate of Figure 9, is determined by subtracting viscous deformations from total deformations for the three ranges of molecular-weight distributions in Figure 8. As predicted from theory, high elastic deformation varies approximately linearly with the logarithm of time up to the point in time where it is essentially fully developed; after that it remains constant. The slopes of the lines are indicated on the graph and show considerable deviation from one another. The experimental average molecular weights and the estimated molecular-weight distribution range are shown in the box at the right. With constant average molecular weight, the slope of high elastic deformation-log time relation increases with extension of the limits of molecular weight distribution. Since this slope is inversely proportional to the high elastic modulus, the narrowest distribution would yield the greatest sensation of stiffness, whereas the widest distribution would appear to have the least resistance to rapid deformation.

*Viscous Deformation and Average Molecular Weight.*—Figure 8 shows that total deformation varies, but viscous deformation or rate of flow remains the

same when a variation of molecular-weight distribution is encountered with constant average molecular weight. The difference between these two deformations—namely, high elastic deformation—is also affected by variations in molecular-weight distributions (Figure 9). Therefore, it appears that the viscous component is a reliable criterion of average molecular weight even when significant differences in molecular weight distributions are encountered.

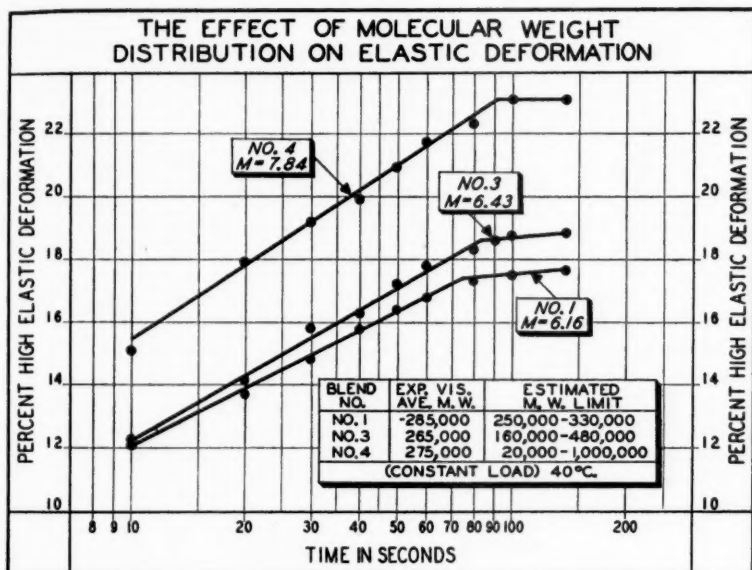


FIG. 9

Dunstan<sup>13</sup> first proposed a relation of viscosity and molecular weight of polymeric substances; this equation took the form:

$$\log \eta = aM + b \quad (5)$$

where  $\eta$  = viscosity;  $M$  = molecular weight.

In measuring the viscosities of linear polyesters above their melting points, Flory<sup>14</sup> showed that over a wide range of molecular weights the logarithm of viscosity is better related to the square root of the weight-average molecular weight. The empirical equation takes the form:

$$\log \eta = A + CM_w^{\frac{1}{2}} \quad (6)$$

where  $M_w$  = weight-average molecular weight.

In discussing the application of Equation 6, it is specifically stated that when a weight average is used, variations in molecular-weight distribution do not affect the viscosity relation. (In this instance the viscosity average is applicable; Flory<sup>6</sup> proposed the term "viscosity average" to distinguish an average molecular weight, calculated from intrinsic viscosities by the equation  $[\eta] = K_1 M^{0.64}$ , from a weight-average molecular weight calculated from intrinsic viscosities by the Staudinger relation  $[\eta] = K_2 M$ .) Instead of isolating the

TABLE II  
MOLECULAR WEIGHT AND RATE OF FLOW

	Viscosity-average molecular weight	$\sqrt{M_v}$	Rate of flow (percentage deformation per second)
Fraction 1	545,000	740	0.00616
2	500,000	707	0.0102
3	440,000	664	0.0207
4	375,000	612	0.0407
5	285,000	532	0.106
6	236,000	486	0.256
7	206,000	454	0.350
8	134,000	365	1.080
9	50,000	224	Not determinable by this method
Blend 1	285,000	532	0.106
3	265,000	515	0.103
4	275,000	524	0.105

viscous component of deformation experimentally as described in this paper, Diene and Klemm<sup>15</sup>, working with vinyl polymers, obtained viscosities from a constant load deformation by calculations from a modified Stefan equation<sup>16</sup>. The logarithm of the viscosities thus obtained was also found to be linearly related to the square root of a weight-average molecular weight.

Table II lists the molecular weights of the individual fractions with their respective square roots and their rates of flow from the slopes of the viscous deformation lines in Figure 10. The molecular weights of the blends of varying distribution are also included with their respective rates of flow. The square roots of the average molecular weights and the logarithms of their respective rates of flow are seen to fit the expression:

$$\log (\text{flow rate}) = a(M_{av})^{\frac{1}{2}} + b$$

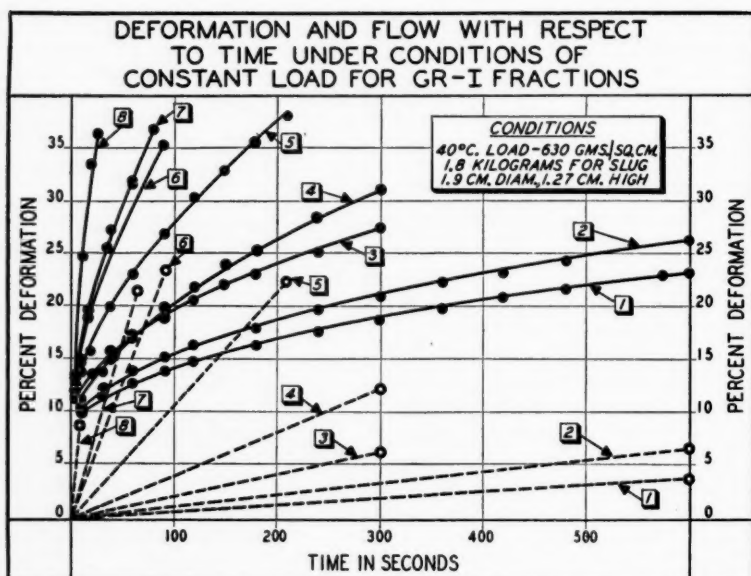


FIG. 10

very closely in Figure 11. From this figure the constants are evaluated so that, specifically, the expression becomes:

$$\log (\text{flow rate}) = -5.83 \times 10^{-3} \sqrt{\bar{M}_v} + 2.16$$

under the specific conditions of the test. Attention is called to the cluster of points marked 1, 3, and 4 which lie on the line and represent the blends of varying molecular-weight distribution.

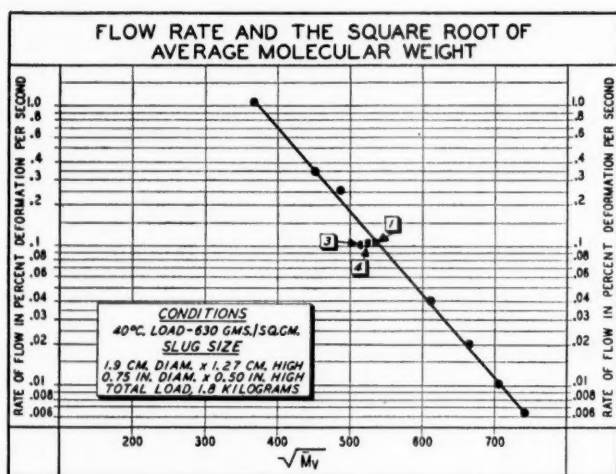


FIG. 11

With this method of measuring total deformation and viscous flow of a polymeric body under conditions of constant load, a relation between rate of flow and molecular weight appears to yield an approximate measure of average molecular weight. The method is independent of molecular weight distribution. In addition, since, for a given average molecular weight, total deformation may vary while viscous flow remains the same, this method also has possibilities of indicating differences in molecular weight distribution in a general way.

#### SUMMARY

A large quantity of a Butyl polymer was fractionated in 100-gram portions into nine relatively narrow molecular weight fractions. The respective fractions from each batch fractionation were combined in solution to obtain sufficient working samples for two types of deformation tests. The fractionation was so designed that the middle fraction of the nine was used as a building block for a series of polymer fractional blends representing equal average molecular weight with gradually increasing molecular weight distribution. The separate fractions and blends of varying distribution were studied in deformation tests involving conditions of both constant rate of deformation and constant load.

Under a constant deformation, at a given rate of compression, and over a temperature range of 40° to 130° C, it was shown that species of very high molecular weight (500,000 viscosity-average molecular weight) require tem-

peratures in excess of 130° C for a transformation to a highly plastic state from one highly elastic. Species of intermediate and low molecular weight (300,000 to 100,000 viscosity-average molecular weight) require progressively lower temperatures for this transformation. Deformations at constant rate, with polymers of constant viscosity-average molecular weight, show the material of narrower molecular weight spread to be the more thermoplastic. A corollary also exists with elasticity; the narrower distribution yields a greater decrease in elasticity when the temperature is increased. Therefore, it can be postulated from the standpoint of equal processing qualities that a narrower distribution of molecular weight can tolerate a higher average molecular weight.

A method has been developed for isolating the elastic and plastic or viscous components of deformation under constant load. Under specific conditions of constant load at 40° C, variations in molecular-weight distribution for a given average molecular weight result in variations in high elastic deformation, while the viscous component remains constant. Thus, increasing the molecular-weight distribution for a given viscosity-average molecular weight tends to yield a softer, more elastic polymer.

Since the viscous component of deformation is independent of molecular weight distribution and depends only on average molecular weight, the constant load deformation test described yields a rapid method of estimating average molecular weight. Rate of viscous flow, which is independent of time if precautions and limitations are observed in the testing procedures, has been determined for individual fractions as well as for blends of varying molecular weight distribution. The logarithm of flow rate is linearly related to the square root of the viscosity-average molecular weight, as suggested by Flory's viscosity equation.

#### ACKNOWLEDGMENT

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## COMPARISON OF NATURAL AND SYNTHETIC HARD RUBBERS \*

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The wartime replacement of natural rubber by synthetics required an unusual expenditure of effort by the hard rubber industry in a short time. At first, curtailment of normal production, coupled with War Production Board restrictions of formulations, mitigated the urgency for synthetic hard rubber research. It soon became evident, however, that a complete line of synthetic hard rubbers would be desirable. These materials could be fabricated with standard rubber processing equipment, and would offer physical and electrical equivalents for the various grades of natural hard rubber developed during nearly a century.

A program was started in these laboratories with the realization that rapid progress might be difficult; research on the compounding of natural hard rubber over the years had failed to produce improvements in overall properties compared with the original "ebonites". The latter, according to the accepted nomenclature<sup>1</sup>, are simple mixtures of rubber with large proportions of sulfur vulcanized by heating until chemical saturation of the rubber is almost complete. The first approach to the problem was through a study of vulcanizing characteristics and through examination of the hard products resulting from the reaction of sulfur with butadiene-styrene copolymers<sup>2</sup>. As the program progressed, the work was extended to cover the processing of GR-S for ebonite fabrication and the compounding of GR-S hard rubbers for specific applications. Studies also were conducted relating to the compounding and processing of hard nitrile rubbers, and new tests were developed to supplement standard procedures used in the physical evaluation of hard rubbers.

Earlier work in these laboratories had indicated that approximate dielectric equivalents of standard hard rubbers could be obtained; the method suggested was direct replacement of first quality smoked sheet rubber with polybutadiene and GR-S synthetic rubbers from both foreign and domestic sources. Earlier work had indicated also that the dielectric properties of these materials could be improved by washing the rubber before compounding to remove water-soluble impurities. The processing characteristics of these materials had revealed that their behavior in production would necessitate a revision of some standard procedures which were being followed in the commercial fabrication of hard rubber.

Stöcklin<sup>3</sup>, Gartner<sup>4</sup>, and Roelig<sup>5</sup> discussed the use of Buna synthetic rubbers in German hard rubber manufacture, and English and Russian interest was shown in the work of Scott<sup>6</sup>, Kashin<sup>7</sup>, and Alexandrov and Lazurkin<sup>8</sup>. These reports disclosed that certain properties of hard products from synthetic rubbers of foreign origin, including resistance to moisture, organic liquids, acids, and to deformation at elevated temperatures, are superior to those of natural

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hard rubbers. Consistently mentioned shortcomings were difficulties in fabrication and a pronounced brittleness in fully cured synthetic hard rubbers.

Limited information on GR-S hard rubbers was published by Cheney and Robinson<sup>9</sup>, who studied various vulcanizates including compounds containing 25 and 35 per cent sulfur. The vulcanization temperature was 157° C, and mention was made of the vigorous evolution of hydrogen sulfide during the cures; this behavior indicated that the reaction involved considerable substitution. Morris and his coworkers<sup>10</sup> described a series of experimental GR-S hard rubbers in which types and proportions of sulfur were varied, and the effects of different fillers and softeners on physical properties were investigated. The compounding and properties of nitrile hard rubbers were described by Garvey and Sarbach<sup>11</sup>.

#### COMPOUNDING AND VULCANIZATION OF GR-S EBONITES

The GR-S used contained 10.76 per cent acetone-extractable matter and 2.50 per cent ash. The iodine number after acetone extraction was 354.3 and the styrene content (ash corrected), as determined from the iodine number, was 21.9 per cent. The unsaturation, as estimated from analytical data by the method of Kemp and Peters<sup>12</sup>, showed that for complete vulcanization at a temperature at which substitution would be minimized, the required sulfur would be approximately 40 parts per hundred of whole polymer. No chemical examination was made of Hycar OS-10, which was a sample of standard material obtained from the Hycar Chemical Company and assumed to have a butadiene-styrene ratio of 50-50. Stauffer tire-brand sulfur was used in all of the experimental mixtures.

Individual batches consisting of 300 grams of GR-S and the required amounts of sulfur were mixed on a water-cooled standard laboratory mill<sup>13</sup>, allowing 10 minutes for mastication and 5 minutes for the addition of sulfur. After overnight storage the batches were given an additional 10-minute remix before vulcanization. None of these compounds mixed on an open mill was sufficiently tacky or free from nerve to be suitable for calendering, plying, and tin plating according to the method employed in processing natural rubber. Compression-type molds faced with tin foil were used to make uniform test sheets. The foil facilitated removal from the molds and assured uncontaminated surfaces for electrical tests.

Sheets  $\frac{1}{8}$ ,  $\frac{1}{4}$ , and  $\frac{1}{2}$  inch thick and 6 inches square were vulcanized in steam platen presses with the temperature carefully controlled. The sheets were cured individually and positive pressure was maintained during vulcanization, to compensate for shrinkage and to eliminate the necessity of surface grinding in the preparation of test specimens. Two-hour intervals were used to study the time effect on the vulcanization reaction and on the resulting products. The lowest vulcanizing time, producing a Rockwell hardness above HR-80 in a half-inch sheet, was utilized to establish the range of cures for each compound.

#### HEAT OF EXOTHERMIC REACTION

The effects of sulfur content and temperature of vulcanization on the exothermic reaction in GR-S ebonites are shown in Figure 1. Cylinders ( $1\frac{1}{2} \times 1\frac{3}{4}$  inches) of GR-S ebonite mixtures, containing 40, 45, and 50 parts by weight of sulfur, were cured in a steel mold placed in the center of steam platens and shielded from external air currents. Iron-constantan thermocouples were

inserted into the center of each specimen through a transite plug in the side of the mold. Similar data were obtained for a natural rubber ebonite of 68:32 composition, because, although this reaction in natural hard rubber has been the subject of a number of investigations, the most recent of which was reported by Church and Daynes<sup>14</sup>, it was considered advisable to obtain a direct comparison under identical conditions. Platen temperatures of 148° and 150° C were used for curing all samples; a cure also was run on the 100:45 GR-S ebonite at 153° C.

With natural rubber and sulfur, compounded in ebonite proportions (68:32) and subjected to a vulcanizing temperature of 148° C, the internal heat formation became evident after 80 minutes and reached a maximum of 170° C after

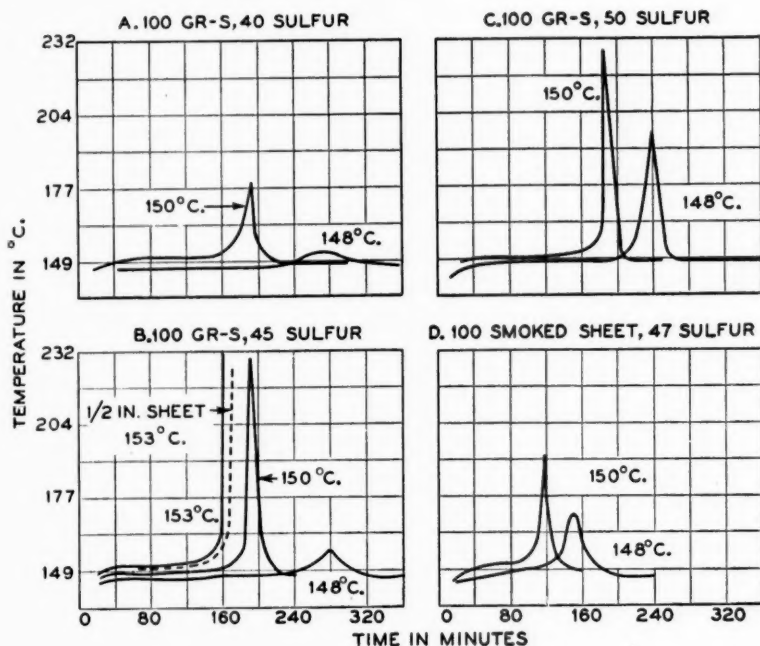


FIG. 1.—Heat of Exothermic Reaction of GR-S and Natural Rubber Ebonites during Vulcanization

138 minutes. Increasing the temperature of vulcanization to 151° C advanced the start of exothermic reaction to 50 minutes; a peak temperature of 191° C was observed at 116 minutes. Sections were cut from the centers of the cured hard rubber cylinders and fractured for examination. The specimens vulcanized at 148° C were dense and free from porosity, whereas the 150° C vulcanizing temperature yielded a porous product, permeated with hydrogen sulfide.

The curves in Figure 1 show that the time required for the beginning of the exothermic reaction is considerably longer for the GR-S than for the natural rubber. The reaction, when it does occur, produces a much higher rise in temperature in the case of the GR-S containing 45 and 50 parts sulfur and vulcanized at 150° C.

## PHYSICAL PROPERTIES

The A.S.T.M. procedures<sup>15</sup> for testing hard rubber products were followed in determining tensile strength, elongation, flexural strength, impact strength (Izod), cold flow, and Rockwell hardness. Measurements of deformation under the conditions of the cold flow test were made at 71° C, and elastic moduli were calculated from load-deflection data taken in conjunction with flexural strength tests. The data for GR-S and Hycar OS-10 ebonites are listed in Tables I and II, respectively. These results show the variations obtainable

TABLE I  
PHYSICAL PROPERTIES OF GR-S EBONITES

Compd.	Sulfur as com- pounded (%)	Cure		% Cold flow		Impact strength (Izod), (ft.-lb. per in.)	Flexural properties, lb. per sq. in.		Tensile strength (lb. per sq. in.)	Elong- ation (%)	Rock- well hard- ness (HR)
		(Hrs.)	(° C)	49° C	71° C		Strength	E* X 10 <sup>4</sup>			
100:25	20.0	16	153	39.3	73.3	1.119	9,130	242	5,980	5.8	83
		20		35.4	48.0	0.963	10,100	263	6,525	4.0	89
		24		26.2	39.4	0.759	10,230	295	7,380	3.9	94
100:30	23.07	8	153	35.8	43.7	0.871	9,300	255	6,670	7.2	83
		10		34.6	45.7	0.932	9,830	265	7,560	6.0	88
		24		2.8	21.6	0.684	12,770	301	8,280	5.4	104
100:35	25.92	6	153	18.0	33.2	0.732	10,570	319	8,380	5.3	92
		8		17.4	35.5	0.661	11,800	296	8,280	5.8	95
		10		5.0	27.1	0.583	11,800	305	7,920	3.9	101
100:40	28.57	6	153	3.0	20.5	0.552	13,070	323	8,740	7.0	103
		8		1.4	9.9	0.523	12,470	317	7,870	5.2	107
		10		1.4	9.5	0.515	14,000	325	9,100	8.5	107
100:45	31.03	8	148	4.7	26.6	0.517	13,300	318	7,570	7.2	103
		10		2.2	17.2	0.501	13,700	323	8,420	4.8	108
		12		2.2	17.8	0.496	13,870	325	8,100	3.2	109
100:50	33.33	8	148	12.0	27.5	0.547	13,030	332	8,325	5.7	101
		10		1.5	11.2	0.562	14,270	337	8,130	3.1	109
		12		1.8	8.4	0.563	14,700	333	7,410	2.4	111
Natural rubber ebonite, 100:47		10	148	2.5	18.0	0.53	15,000	330	10,000	4.0	99

\*  $E$  = Modulus.

TABLE II  
PHYSICAL PROPERTIES OF Hycar OS-10 EBONITES

Compd.	Cure		% Cold flow		Impact strength (Izod), (ft.-lb. per in.)	Flexural properties, lb. per sq. in.		Tensile strength, (lb. per sq. in.)	Elongation (%)	Rock- well hard- ness (HR)
	(Hrs.)	(° C)	49° C	71° C		Strength	$E \times 10^3$			
100:30	4	153	21.3	44.8	0.485	14,200	368	9,310	7.7	100
	6		1.4	21.9	0.491	15,800	364	8,670	5.0	109
	8		1.7	26.7	0.483	15,300	360	10,700	6.7	107
100:35	4	148	37.3	54.8	0.502	11,500	341	9,350	4.0	92
	6		3.6	28.8	0.500	14,500	363	9,400	4.1	104
	8		0.8	2.7	0.441	12,200	392	10,850	6.3	113
100:40	4	148	2.2	25.6	0.500	14,400	376	9,980	4.3	105
	6		1.1	13.9	0.499	12,900	376	10,800	5.8	110
	8		0.4	1.4	0.507	17,100	359	10,610	4.3	116
100:45	4	148	1.4	12.4	0.448	16,400	399	9,540	5.0	110
	6		0.5	1.7	0.332	17,800	339	10,740	5.4	116
	8		0.3	0.7	0.352	12,400	387	11,340	6.0	118

through changes in sulfur content and time of cure. Changes produced by continued heating are particularly evident in the GR-S ebonites compounded with less sulfur than is required for theoretical saturation. There is a striking similarity between the overall properties of the GR-S ebonites compounded with 40 or more parts of sulfur per hundred of whole polymer, and the corresponding data for a fully cured natural ebonite. The fully cured Hycar OS-10 ebonite compounded with 40 parts of sulfur appears to be superior.

The Rockwell hardness values for the GR-S ebonites are higher than those commonly observed in natural ebonites, and a reduction in impact strength is evident in the Hycar OS-10 ebonite of 100:45 composition; but none of the other measured properties furnishes any indication of the brittleness mentioned by European investigators. Brittleness is known to exist in these materials through observations made in the course of preparing test specimens.

To add further significance to the differences in Rockwell hardness, penetration and recovery measurements after 15-second intervals were made on a series of GR-S ebonites compounded with different sulfur contents, in comparison with a natural ebonite of 100:47 composition. Using the conditions specified by the Rockwell hardness test for hard rubber, the data in Table III were

TABLE III  
BRITTLINESS AND PENETRATION RECOVERY OF GR-S AND  
NATURAL RUBBER EBONITES

Compn.	Brittleness breaking angle for $\frac{1}{8}$ -in. strips deflected 6° per sec., degrees	Tests with $\frac{1}{8}$ -in. specimens and $\frac{1}{4}$ -in. ball	
		Penetration†	Residual deformation
GR-S: sulfur			
100:35	39	121.5	26
100:40	30	115.0	21
100:45	27	115.0	22
100:50	26	108.0	19
Natural ebonite:			
sulfur, 100:47	90*	116.0	31

\* Specimen did not break.

† One scale division = 0.002 mm.

obtained. They demonstrate that GR-S ebonites containing 40 and 45 parts of sulfur are penetrated to approximately the same depth as the natural ebonite. Their tendency toward instantaneous recovery when the load is removed is of a higher order than that of the natural ebonite. The GR-S ebonite of 100:35 composition is somewhat less resistant to penetration than the natural ebonite; nevertheless it exhibits a greater recovery on removal of the deforming load. Increasing the sulfur content to 50 parts per hundred of GR-S increases the resistance to penetration to a marked degree and effects also a further reduction in the deformable phase.

The similarity of impact strength values for the natural and GR-S ebonites might lead to the assumption that strips of natural and synthetic ebonites of equal thickness can be bent to the same degree before breaking. A discussion in the literature of the brittleness of ebonite<sup>16</sup> was based on the results of Charpy impact tests. If, however, brittleness is defined as the degree of bending that a given material withstands at 25° C before breaking, instead of as the energy a supported sample absorbs from a pendulum before breaking, a fundamental difference between natural and synthetic products becomes evident.

Several methods were investigated for determining the degree to which natural and synthetic ebonites can be bent before fracture occurs. The apparatus shown in Figure 2 was used to apply a sharp bend over a constricted area to test-specimens  $\frac{1}{2} \times \frac{1}{8}$  inch in cross section. Table III compares the bending properties of natural and GR-S ebonites as made by this method. Another type of equipment used for brittleness tests was the Olsen-Tour-Marshall stiffness tester<sup>17</sup>. Although it was primarily designed for measuring

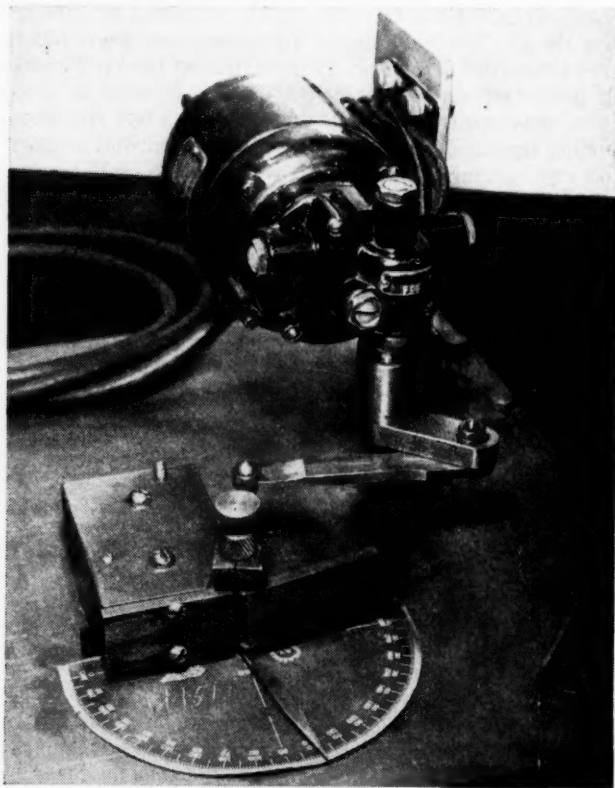


FIG. 2.—Apparatus for Brittleness Testing of Hard Rubbers. Strips  $\frac{1}{2}$  inch wide and  $\frac{1}{8}$  inch thick are broken by bending at  $6^\circ$  per second

modulus in flexure of a rigid material, this tester was adapted to the quantitative measurement of brittleness by the use of a  $\frac{1}{8}$ -inch span. Figure 3 shows typical results comparing the stiffness, *A*, and brittleness, *B*, of natural and GR-S ebonites.

It appears that the ability to withstand a sharp bend is characteristic of natural ebonites and is not obtainable in GR-S ebonites, even if the latter have a relatively low sulfur content. Unsuccessful attempts were made to improve this property of GR-S ebonites by the use of selenium, which is claimed to produce an elastic phase incapable of conversion to the hard state, and by the use of polymeric plasticizers such as polyisobutylene, Butyl rubber, and a

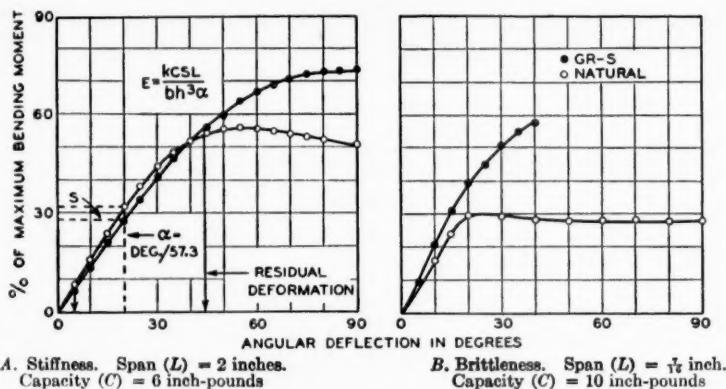


Fig. 3.—Tour-Marshall Tests on GR-S and Natural Rubber Ebonites.

sulfur vulcanizable polyester (Paraplex S-200). It is of interest to note, however, that exposure at low temperatures reverses the order of brittleness in the natural and GR-S ebonites. After a 24-hour conditioning period at  $-30^{\circ}\text{C}$  the natural ebonite fractured when it was bent  $12^{\circ}$ , while the brittleness of a GR-S ebonite was unchanged.

The heat deformation of natural and synthetic ebonites was investigated by means of a parallel plate plastometer with electrically heated platens, and by a deforming load of 900 pounds per square inch applied for one hour. The materials examined included natural and GR-S ebonites of 100:46.5 and 100:45

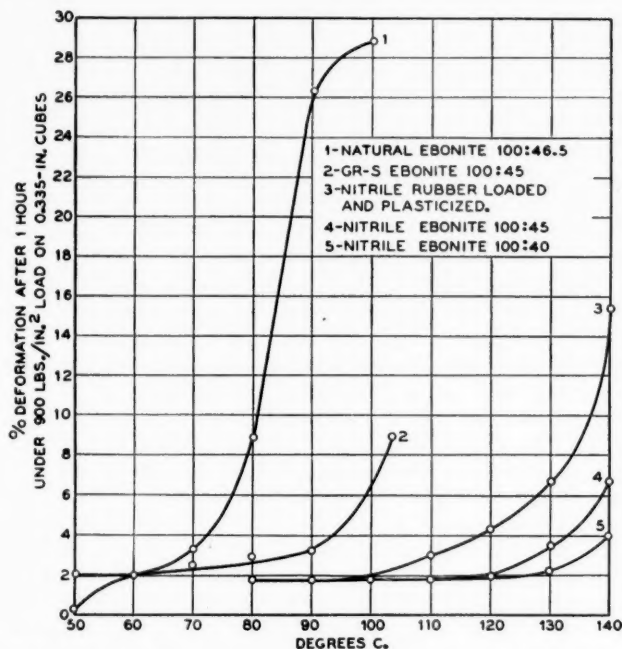


Fig. 4.—Flow Characteristics of Natural and Synthetic Hard Rubbers.



composition, respectively, and nitrile ebonites of 100:40 and 100:45 composition. The latter were compounded with a nitrile copolymer containing 26 per cent acrylonitrile. In view of the difficulties encountered in the fabrication of nitrile ebonites, one of these materials containing 10 parts by weight of Naftolen R-100 was included in the series. The temperature-deformation curves in Figure 4 show that the natural ebonite is superior to the GR-S hard product below 60° C, but above this temperature the reverse is true. The superior heat deformation of the nitrile ebonites also is evident, but the adverse effect of using a plasticizer to improve the working properties is obvious.

### CHEMICAL STABILITY

The effect of heat on the rate of hydrogen sulfide evolution from natural and GR-S ebonites was determined according to a procedure followed by previous investigators<sup>18</sup>. The apparatus consisted of a glass tube with an enlarged section for the samples, and connecting inlet and outlet tubes of smaller diameter for the passage of nitrogen over the ebonite. The outlet tube was fused to the sample container, and the inlet tube connected by a ground glass joint. A glass wool filter pad at the exit end of the sample tube prevented any of the material from being swept into the precipitation bottle. The apparatus was mounted in an oven, and commercially pure nitrogen was passed through a 25-foot coil of stainless steel tubing which was also enclosed in the oven. A Fisher-Milligan bubble tower, containing a saturated solution of lead acetate acidified with acetic acid, was connected to the exit end.

The temperatures at which perceptible lead sulfide precipitates formed during a 2-hour exposure were determined with this assembly; 2.5-gram samples were removed with a wood rasp from fully vulcanized half-inch-thick ebonite sheets. The natural ebonite (100 smoked sheet, 46.5 sulfur, cured 11 hours at 148° C) exhibited no appreciable signs of decomposition during 2-hour periods at 93° and 99° C. At 104° C, however, a lead sulfide precipitate was visible at the tip of the exit tube in the bottom of the bubble tower. At 116° and 127° C lead sulfide appeared in appreciable quantities throughout the tower. A fresh sample placed in the heating tube for 2 hours at 138° C resulted in the formation of 0.040 gram of lead sulfide.

A similar examination of GR-S ebonite (100 GR-S, 45 sulfur, cured 11 hours at 148° C) produced only a slight visible formation of lead sulfide. At 143° C some decomposition was evident in a two-hour heating period, and at 149° C the lead sulfide precipitate from a 9.5-hour test weighed 0.039 gram, approximately the decomposition observed for natural ebonite in 2 hours at 138° C.

A nitrile ebonite sample (100 Perbunan, 42 sulfur, cured 10 hours at 142° C) was more unstable than the natural and GR-S ebonites. The first noticeable lead sulfide formation from this material occurred at 99° C; after 9.5 hours at 149° C the weight of the precipitate was 0.174 gram.

The relative chemical stabilities of natural and GR-S hard rubber dusts were tested by storing samples of similar particle size in a closed container in the presence of, but not in contact with, lead acetate-impregnated filter paper; the samples were examined at intervals during a 2-month period. Progressive darkening of the paper indicated that the rate of hydrogen sulfide evolution was decidedly more rapid from the natural hard rubber dust. After one hour a noticeable reaction was apparent on the edges and exposed side of the paper over the natural dust, but no discoloration was observed in that over the GR-S. After 2 months the reaction of hydrogen sulfide with lead acetate over the

GR-S dust was barely evident, while the same exposure to the natural dust produced a lustrous gray-black formation over the entire exposed section of the indicator paper.

#### DUST-FILLED GR-S HARD RUBBERS

Hard rubber dust has long been used in the fabrication of thick articles, mainly because it dilutes a given mixture and reduces the exothermic heat of reaction during vulcanization. Its use results in materials which are satisfactory dielectrics and can be machined easily, although they are of reduced physical quality. Hard rubber dust also lowers the cost of articles when reduced quality is commensurate with ultimate application.

At first, commercial-type hard rubbers containing GR-S were compounded with whole-tire reclaimed rubber and natural hard rubber dust (Table IV, compound A). Vulcanizates of this kind, however, proved to be extremely brittle and subject to excessive deformation under the conditions of the cold flow test. As GR-S became more available and the supply of natural hard rubber dust was exhausted, formulas were investigated in which the reclaimed rubber was eliminated and GR-S ebonite dust replaced the corresponding natural product (Table IV, compound F). The composition listed contains the minimum quantity of dust required to impart satisfactory processing characteristics to an open-roll-mill mix; the sulfur content shown produces a suitable compromise between cold flow and impact strength.

Further studies on GR-S dust-filled hard rubbers, using hot processed copolymers, indicates that commercial compounds can be produced adequately with smaller amounts of dust, in applications where retention of shape and elimination of blowing during vulcanization require its use. However, GR-S dust in quantities as low as 5 parts by weight causes an appreciable increase in brittleness.

#### MINERAL-FILLED GR-S HARD RUBBERS

Experimental compounds, prepared primarily to investigate the possibilities of improving the working properties of GR-S hard rubbers, covered the range of mineral fillers commonly used in the rubber industry. With the cool open-roll-mill mixing technique, only one ingredient, a diatomaceous earth designated as Celite-270, had a favorable effect on processing characteristics. The minimum quantity required to produce a stock that could be calendered without excessive shrinkage was 50 parts by weight on the whole polymer. Further compounding experiments with formulations based on GR-S and Celite in these proportions resulted in the development of commercially adaptable compounds which have found extensive use. A typical formula of this type is listed in Table IV (compound E).

A GR-S whiting-filled hard rubber compound suitable for fabrication of sheets (compound D, Table IV) was examined for electrical surface stability after exposure to ultraviolet light, in comparison with a whiting-filled natural hard rubber and the corresponding natural ebonite. Exposure was by a General Electric S<sub>4</sub> sunlamp at a distance of 12 inches; the surface resistance was measured with a high sensitivity galvanometer by the direct deflection method at 30° C and 90 per cent relative humidity. The surface resistivity of a GR-S ebonite of 100:45 composition previously had been determined as  $3.3 \times 10^6$  ohms after 110 hours, at which time the test had been discontinued because of the low value. After 800-hours' exposure, the whiting-filled natural

TABLE IV  
TECHNICAL FORMULATIONS OF SYNTHETIC HARD RUBBERS

Ingredients, parts by wt.	GR-S reclaim dust-loaded hard rubber A		GR-S hard rubbers				Nitrile hard rubbers	
	Flexible ebonite B	Ebonite C	Whiting-filled D	Celite-filled E	Dust-filled F		Celite-filled G	Ebonite H
GR-S, type CA	100.0	100.0	100.0	100.0	100.0		..	..
GR-S, type AC	..	..	..	..	..		100.0	..
Nitrile rubber, 26% acrylonitrile	..	..	..	..	..		..	100.0
Nitrile rubber, 39.5% acrylonitrile	121.5	..	..	..	..		..	..
Reclaimed rubber, 62% rubber hydrocarbon	85.75	37.5	37.5	39.0	40.0		42.5	35.0
Sulfur, tire brand	..	..	..	..	..		10.0	3.0
Sulfur, micronized SC	40.0	..	..	..	..		..	..
Magnesium oxide, LC	3.0	3.0	3.0	..	3.0		..	..
Hard rubber dust, natural	200.0	..	..	..	50.00		..	..
Hard rubber dust, GR-S	..	..	100.0	..	..		50.0	..
Atomite whiting	..	..	..	..	..		10.0	..
Celite-270	..	..	..	..	..		..	..
Naftolen R-100	32.3	..	15.0	12.0	12.0		..	..
O.E.I. (dodecyl mercaptan)	..	..	..	..	..		..	..
Synsepi-N	..	2.0	..	..	..		..	..
G-25 plasticizer	..	..	..	..	..		..	10.0
Total	539.55	145.0	142.5	255.5	201.0	205.0	212.5	148.0
Vulcanization Time (hrs.)	11	11	11	11	11	11	10	10
Temperature (°C)	148	148	148	148	148	148	142	142
Physical properties								
Cold flow (%)	16.6	2.2	1.8	1.4	7.6		0.46	0.50
49°C	40.0	14.8	11.0	15.9	27.1		1.38	0.85
71°C	10,600	14,900	13,900	11,800	9,000		..	11,700
Flexural strength (lb./sq. in.)	369,000	312,000	298,000	303,000	355,000		..	335,000
Modulus (lb./sq. in.)	0.265	0.465	0.415	0.463	0.313		..	0.398
Izod impact strength (ft.-lb./in. of notch)	12	42	30	25	20		16	22
Brittleness, degrees to break	32	> 90	5.5	..	..		..	..
0.062 × 0.50 in.								
0.031 × 0.50 in.								

and whiting-filled GR-S hard rubbers exhibited surface resistivity values of  $3.4 \times 10^8$  and  $3.8 \times 10^7$  ohms, respectively, as compared to  $4.8 \times 10^6$  ohms for the natural ebonite after 800 hours and  $3.3 \times 10^5$  ohms for the GR-S ebonite after 110 hours. On the basis of these tests, although the surface resistivities of both the whiting-filled GR-S hard rubber and the GR-S ebonite are lower than that of the natural products, the improvement brought about by whiting is significant.

## DIELECTRIC PROPERTIES

Equipment and methods described in an earlier publication<sup>19</sup> were used in most of the dielectric tests. The power factor and dielectric constant of GR-S and Hycar OS-10 ebonites were measured at 1, 10, and 100 kilocycles, with the test temperature at 25° C and the relative humidity equal to or less than 40 per cent. The variation of dielectric constant and power factor with frequency and sulfur content of the GR-S and Hycar OS-10 ebonites as shown in Table V.

TABLE V  
VARIATION OF DIELECTRIC PROPERTIES OF NATURAL AND SYNTHETIC HARD RUBBERS WITH SULFUR CONTENT AND FREQUENCY AT 25° C

	Sulfur content (%)	Dielectric constant					Power factor (%)				
		1 ke.	3 ke.	10 ke.	30 ke.	100 ke.	1 ke.	3 ke.	10 ke.	30 ke.	100 ke.
GR-S ebonites, cured 8 hrs. at 153° C.	20	2.86	..	2.84	..	2.82	0.48	..	0.43	..	0.53
	23	2.85	..	2.84	..	2.82	0.39	..	0.37	..	0.47
	26	2.94	..	2.91	..	2.89	0.68	..	0.55	..	0.63
	29	2.98	..	2.95	..	2.93	0.66	..	0.56	..	0.61
	31	2.97	..	2.94	..	2.92	0.67	..	0.56	..	0.64
Hycar OS-10 ebonites, cured 8 hrs. at 153° C	23	2.94	..	2.92	..	2.92	0.31	..	0.34	..	0.44
	26	2.87	..	2.86	..	2.85	0.31	..	0.33	..	0.48
	29	2.86	..	2.84	..	2.83	0.31	..	0.33	..	0.40
	31	2.91	..	2.89	..	2.88	0.36	..	0.35	..	0.39
Nitrile hard rubbers, cured 10 hrs. at 142° C											
Compound G, Table IV	30	3.81	3.77	3.71	3.65	3.58	1.62	1.79	2.10	2.44	2.79
Compound H, Table IV	26	3.94	3.89	3.80	3.72	3.61	3.03	2.83	3.09	3.37	3.53
Natural rubber ebonites <sup>20</sup> , cured 25 to 40 hrs. at 140° C	20	2.73	2.72	..	..	2.70	0.30	0.35	..	..	0.58
	23	2.73	2.72	..	..	2.70	0.25	0.33	..	..	0.63
	26	2.76	2.75	..	..	2.74	0.32	0.39	..	..	0.74
	29	2.79	2.78	..	..	2.75	0.42	0.48	..	..	0.75
	32	2.82	2.81	..	..	2.78	0.43	0.47	..	..	0.72

Data on hard nitrile rubbers as well as data of Scott, McPherson, and Curtis<sup>20</sup> on natural rubber ebonite are included for comparison. The sulfur content of GR-S, Hycar OS-10, and natural rubber ebonites appears to have only a small effect on dielectric properties under the given conditions. The change in dielectric constant and power factor with time of cure of the GR-S and Hycar OS-10 ebonites also is slight, as indicated in Table VI. Dielectric constant increases between 4- and 8-hour cures probably are due to increases in combined sulfur. The power factor of the Hycar OS-10 ebonites is lower than that of the GR-S but increases to a small extent directly with curing time.

The dielectric constant and power factor of one GR-S hard rubber were measured over a frequency range of 1 kilocycle to 14 megacycles. Measurements from 100 kilocycles to 14 megacycles were made on a type 160-A Q-meter, with a substitution condenser designed by Yager<sup>21</sup> of these laboratories. The data are plotted in Figure 5 with corresponding data on a natural hard rubber. The sulfur content of the GR-S is slightly higher than that of the natural rubber.

TABLE VI

VARIAION OF DIELECTRIC PROPERTIES OF GR-S AND Hycar OS-10 EBONITES WITH SULFUR CONTENT AND TIME OF CURE AT 1 KILOCYCLE AND 25° C

	Sulfur content (%)	Dielectric constant						Power factor (%)					
		4 hr.*	6 hr.	8 hr.	10 hr.	16 hr.	24 hr.	4 hr.*	6 hr.	8 hr.	10 hr.	16 hr.	24 hr.
GR-S	20	2.84	..	2.86	..	..	2.84	0.38	..	0.48	..	..	0.38
	23	..	..	2.85	..	2.91	3.01	..	..	0.39	..	0.39	0.46
	26	2.90	2.89	2.94	..	..	..	0.65	0.69	0.68	..	..	..
	29	..	2.93	2.98	2.99	..	..	..	0.61	0.66	0.63	..	..
	31	2.91	2.96	2.97	..	..	..	0.74	0.65	0.67	..	..	..
Hycar OS-10	23	2.83	2.82	2.94	..	..	..	0.22	0.26	0.31	..	..	..
	26	2.79	2.85	2.87	..	..	..	0.20	0.29	0.31	..	..	..
	29	2.82	2.90	2.86	..	..	..	0.20	0.31	0.31	..	..	..
	31	2.82	2.93	2.91	..	..	..	0.24	0.35	0.36	..	..	..

\* Time of cure at 153° C.

The latter had been dried over phosphoric anhydride for a month before test, whereas the GR-S sample had been kept in the laboratory at a relative humidity of 40 per cent or less; hence the dielectric constant and power factor of the GR-S may be even lower than those shown.

It is evident that the dielectric behavior of natural and GR-S hard rubbers is similar. Both show a region of dielectric absorption spanning the greater part of the given range of frequencies. The dielectric constant decreases slowly but steadily with increasing frequency, and the power factor rises to a

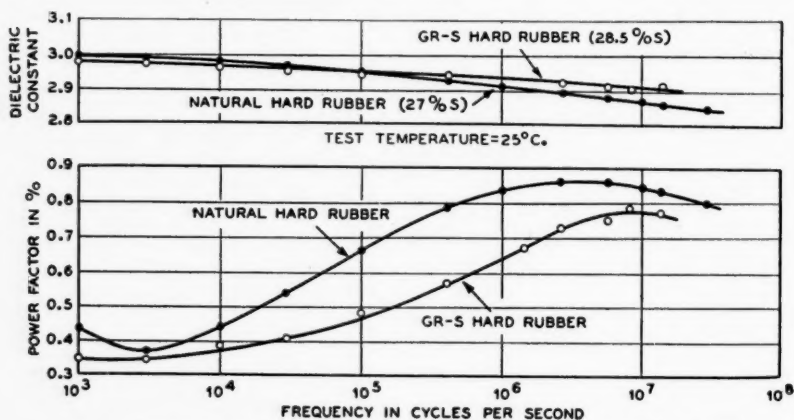


Fig. 5.—Frequency Variation of Dielectric Constant and Power Factor of GR-S and Natural Rubber Ebonites

maximum in the neighborhood of  $3 \times 10^6$  cycles for natural rubber and  $10^7$  cycles for GR-S. This dielectric absorption is small compared to that found at higher temperatures by Kitchin<sup>22</sup> and by Scott, McPherson and Curtis<sup>20</sup>. The data show that at 25° C GR-S hard rubber has at least as good insulating characteristics as natural hard rubber over a wide frequency range.

#### PROCESSING AND COMPOUNDING STUDIES

The synthetic ebonites prepared and examined as described serve to define the overall properties obtainable; the fact that special techniques were required to produce them, however, led to an intensive study of the processing



characteristics of GR-S and nitrile copolymers, to determine which of these base materials were best suited for commercial ebonite fabrication. Since Banbury breakdown is factory practice, this method was used in studies of the effect of time and temperature as well as addition of organic compounding ingredients as processing aids.

The Banbury-processed materials were worked for 5 minutes in 325-cc. portions from 1000-cc. batches on a 6 × 12 inch roll mill set for 0.040-inch clearance under constant conditions; the materials were sheeted on the front roll by gradual opening until the bank disappeared. The samples then were cut squarely across, placed on a talced surface, and measured 5 minutes after removal to determine shrinkage. A 20-minute breakdown at 149–163° C with Naugatuck GR-S produced a base material having a shrinkage figure of 27 per cent. One of the softest GR-S copolymers available, which forms a hole-free band in several passes through the open rolls, was found to shrink 55 per cent. This sample was from the Firestone Lake Charles plant and was similar in open-roll-mill behavior to the GR-S used in the earlier experiments. A number of GR-S samples from other sources exhibited shrinkage values intermediate between those of the two extremes cited. The GR-S most favorable for hot Banbury processing was extremely difficult to work on open rolls, requiring 10 minutes to produce a hole-free band.

The GR-S copolymer showing the most favorable breakdown as judged by shrinkage test was compounded with sulfur and put through the standard processing operations of calendering, ply building, tin plating, and vulcanization under water in the autoclave. The need for more surface tackiness was evident but other conditions were favorable. This deficiency was overcome by addition of a small quantity of magnesium oxide and small quantities of chemical plasticizers. One of these processing aids, dodecyl mercaptan, had a beneficial effect on the brittleness of the vulcanizate, for two parts by weight with a specially processed sulfur (Table IV, compound *B*) gave an ebonite of low cold flow which could be bent through an angle of 90° in thin strips. Another chemical plasticizer, Synpep N, also proved of value (Table IV, compound *C*). Two parts by weight added at the end of the mix resulted in a pronounced tack favorable to building operations. The same quantity incorporated with the GR-S at the start of the processing cycle completely inhibited the breakdown and produced a material which, although soft and tacky, had a shrinkage of 60 per cent.

Similar studies were conducted on nitrile copolymers with variable acrylonitrile content. The base material most suitable for ebonite compounding, as judged by freedom from shrinkage, was Hycar OR-15, a copolymer containing 39.5 per cent acrylonitrile. Data on the nitrile copolymers are plotted in Figure 6 and show temperature, power consumed, and shrinkage of the milled materials. One 39.5 per cent compound was milled at the minimum temperature required for breakdown; the other was milled at hot breakdown.

When the nitrile ebonite mixture prepared with Hycar OR-15 was compounded with 35 parts by weight of sulfur and broken down for 30 minutes at the elevated temperature, it was dry and leathery but could be calendered smoothly on rolls at 66° C. Other studies directed toward adding the necessary tack to the nitrile ebonite mixture resulted in selection of a polyester plasticizer of low molecular weight, Paraplex G-25. Adding 10 parts by weight to the 100:35 nitrile ebonite base produced a stock (Table IV, compound *H*) that could be tin-plated and built up into thick sheets without ply separation. As a further guide to the selection of the most suitable nitrile hard rubber com-



pound for general use, open-roll mixtures were made using one of the softer rapid banding copolymers (Perbunan containing 26 per cent acrylonitrile) compounded with Celite-270 and other ingredients as shown (Table IV, compound G). This compound, although it could be calendered, plied, and plated did not have any advantages over the plasticized ebonite. The latter offers the most satisfactory approach to the commercial sheet fabrication of nitrile hard rubber.

Vulcanization experiments on tin-plated hard nitrile rubber sheets under water in the autoclave indicated that this process requires unusual precautions. At a vulcanizing temperature of 148° C surface decomposition was evident after 6 hours, considerably short of the time required to produce the maximum

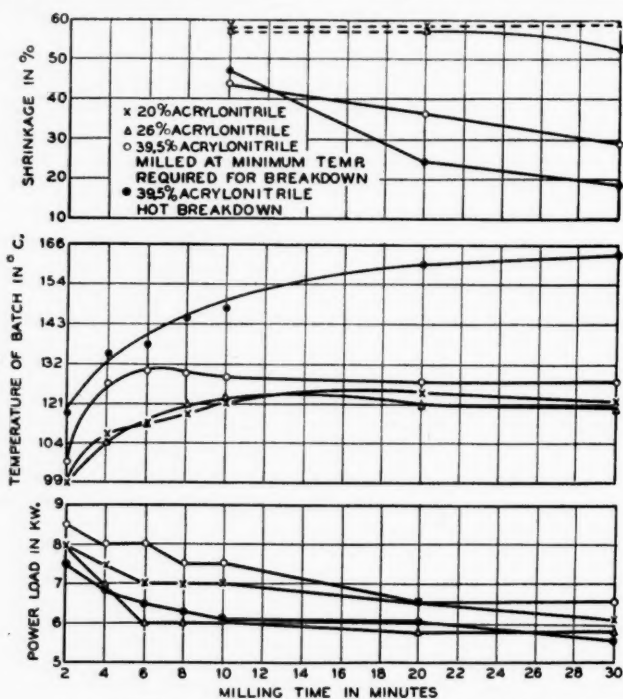


Fig. 6.—Milling study of Nitrile Rubber for Ebonite Fabrication  
1000-cc. batches processed in No. 0 Banbury

resistance to deformation at elevated temperatures in an unaccelerated compound. Decomposition was eliminated by using a vulcanizing temperature of 142° C. This has become the standard practice of these laboratories in nitrile ebonite vulcanization. It is important that perfect contact be made between the tin and calendered sheet in the plating operation before vulcanization, as the conditions of autoclave vulcanization are favorable to the hydrolysis of the cyanide groups in the acrylonitrile copolymer. Ammonia generated by this reaction would be damaging.

#### EFFECTS OF HOT MASTICATION

Certain changes in the structure of the synthetic copolymers undoubtedly result from the prolonged hot breakdown necessary to facilitate the fabrication

of ebonites. It may be assumed that the chain molecular length is shortened and the gel contents increased by this treatment; furthermore the overall reactions during vulcanization with sulfur might be different among copolymers thus treated, and the same materials prepared by mixing on a cool open-roll mill. Determinations of unsaturation showed no significant change in samples taken from a batch of GR-S originally and after 10, 20, and 30 minutes of hot Banbury mastication. Using the Kemp-Wijs method the values were 332.8, 333.5, 333.9, and 332.8, respectively, for the periods mentioned.

The physical test values determined for the GR-S ebonites prepared from hot processed copolymer (compounds *B* and *C*, Table IV) are of a high order. The fact that the commercial type of formula (compound *C*, Table IV) developed the properties listed, with a sulfur content of 37.5 parts per hundred of whole polymer, may be attributed to ingredients other than the GR-S and sulfur; or it may be taken as an indication that a lower sulfur ratio is advisable in compounding ebonites in which the GR-S has been subjected to hot breakdown. Processors of soft rubber may be surprised that this extensive breakdown of the basic copolymers has little effect on the ultimate physical properties of synthetic ebonites, since a similar technique in the fabrication of soft products results in a marked reduction in tensile strength, elongation, and other mechanical properties.

#### INTERMEDIATE COMPOSITIONS OF GR-S AND SULFUR

A mixture consisting of 100 parts of GR-S and 25 parts of sulfur vulcanized 16 hours at 153° C was the first material of the series that could be evaluated by conventional test methods; nevertheless, lower cured products of this composition as well as those of a 100:20 GR-S and sulfur mixture are of interest in view of certain needs for flexible leatherlike materials. These needs are now being filled by plasticized polyvinyl chloride and other compounded flexible plastics.

Cheney and Robinson<sup>9</sup> reported that the relation between sulfur content and tensile strength of GR-S vulcanizates shows a progressive increase, and that above 10 per cent combined sulfur, the increase in tensile strength is substantial. Data of Houwink<sup>23</sup> for vulcanizates of natural rubber and sulfur indicates a maximum tensile strength at 5.5 to 6.0 per cent combined sulfur, and a falling off to a minimum value at 12 per cent combined sulfur with no marked increase until after 25 per cent. The high tensile strength of natural pure-gum rubbers in the low sulfur range contrasts sharply with the low tensile strength of the corresponding GR-S gum stocks.

Natural rubber vulcanizates compounded with sulfur varying from 15 to 25 parts by weight (13 to 20 per cent) were examined by Gibbons and Cotton<sup>24</sup> as possible substitutes for leather and compounded soft rubber soling stocks. Their work showed that accelerated compounds containing 17.5 parts by weight of sulfur exhibit the highest original physical properties, and that unaccelerated compounds cured with 22.5 to 25.0 parts of sulfur have the best aging properties but are not sufficiently stable under accelerated aging conditions to warrant their use. No marked improvements are obtained by the use of antioxidants.

Rubber-sulfur vulcanizates are shown by Kemp<sup>25</sup> and later by Scott, McPherson, and Curtis<sup>26</sup> to vary widely in dielectric properties at 25° C and 1 kilocycle in the intermediate ranges of combined sulfur. Kemp's data indicated a maximum in dielectric constant (3.95) at 10 per cent combined sulfur, compared to 3.2 at 5 per cent in the soft rubber range and 2.7 when 19 per cent sulfur is combined with the rubber. The power factor reached a

maximum of 0.098 at 13 per cent combined sulfur and a value of 0.005 at 19 per cent, compared to 0.014 at 5 per cent.

From the information given on the intermediate products of natural rubber and sulfur it appears that their rapid deterioration on aging is the main objection to their commercial use. Although our investigation of GR-S-sulfur vulcanizates below the ebonite range was limited, there is evidence that some of these materials may be of interest in applications where their specific properties are advantageous. The effect of sulfur content on the dielectric properties of flexible GR-S vulcanizates (Table VII) indicates that the 1-kilocycle di-

TABLE VII  
DIELECTRIC PROPERTIES OF GR-S INTERMEDIATE VULCANIZATES AT 25° C

Sulfur		Vulcanization†		Dielectric constant (1 kc.)	Power factor (%) (1 kc.)	D.C. vol. resistivity (400 volts)
Parts*	(%)	(Hrs.)	(° C)			
6	5.7	12	148	3.09	0.56	> 10 <sup>16</sup>
12	10.7	12	148	3.46	4.78	> 10 <sup>16</sup>
14	12.3	12	148	3.38	6.18	> 10 <sup>16</sup>
16	13.8	12	148	3.19	6.06	> 10 <sup>16</sup>
18	15.3	12	148	3.05	4.59	> 10 <sup>16</sup>
20	16.7	12	148	3.03	4.35	> 10 <sup>16</sup>
20	16.7	8	153	3.02	4.17	10 <sup>16</sup>
20	16.7	24	153	2.84	0.87	6 × 10 <sup>16</sup>

\* By weight to 100 of whole polymer.

† 1/8-inch calendered sheets, tin-plated and vulcanized under water in open steam.

electric constant and power factor reach maximum values with 12 and 14 parts of combined sulfur, respectively. The power factor remains high throughout the range of flexible products, but upon conversion of the 100:20 composition to a hard product by prolonged heating at 153° C, the power factor drops to 0.87 per cent and the dielectric constant to 2.84.

Table VIII contains physical test data for intermediate products of GR-S and smoked sheet rubber vulcanized at 148° C and for an accelerated GR-S and

TABLE VIII  
PHYSICAL PROPERTIES OF INTERMEDIATE VULCANIZATES OF GR-S AND SMOKED SHEET RUBBER

Composition	Vulcanization		Tensile strength (lb./sq. in.)	Elongation (%)
	Time	° C		
GR-S 100, sulfur 20	8 hr.	148	2100	115
	12 hr.	148	2200	110
	16 hr.	148 orig.	2900	85
	16 hr.	148 aged*	2930	76
	24 hr.	148	3740	65
	36 hr.	148	5060	28
GR-S 100, sulfur 20, Altax 1, Zimate 1	4 min.	200 orig.	1500	100
	4 min.	200 aged*	2100	76
	6 min.	200	2225	70
	8 min.	200	2900	67
Smoked sheet 100, antioxidant 2, sulfur 21	16 hr.	148 orig.	2920	205
	16 hr.	148 aged*	525	0†
	36 hr.	148	2950	200

\* Specimens aged 48 hrs. in oxygen bomb at 70° C and 300 lb. per sq. in. oxygen pressure.

† Oxidized surfaces developed cracks immediately upon application of load.

sulfur mixture cured at 200° C. A significant difference in the natural and GR-S compositions may be seen in the data for the 16- and 36 hour cures. The tensile strength and elongation of the natural rubber composition undergo practically no change, whereas the extended cure converts the GR-S vulcanizate from a flexible to a hard product of high tensile strength and relatively low elongation. However, the GR-S product cured 16 hours exhibited little change in physical properties or appearance after 2 days of aging in an oxygen bomb. The corresponding natural rubber was converted to an unextensible product of exceedingly brittle surface and visibly deteriorated internal structure.

## ACKNOWLEDGMENT

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# PROPERTIES OF HARD RUBBER. XVI. INFLUENCE OF RUBBER-SULFUR RATIO AND VULCANIZATION TIME ON THE PROPERTIES OF PURE RUBBER-SULFUR COMPOSITIONS. (2)

## MECHANICAL AND ELECTRICAL PROPERTIES \*

H. F. CHURCH AND H. A. DAYNES

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### I (a). B. METHODS OF TEST AND RESULTS

#### 4. TENSILE STRENGTH AND BREAKING ELONGATION; STRESS-STRAIN RELATIONSHIP; YOUNG'S MODULUS; RESILIENT ENERGY.

(a) *Methods of Test.*—(i) and (ii) Tensile Strength and Breaking Elongation; Stress-Strain Relationship. All the materials were tested for tensile strength in addition to cross-breaking, which is a less fundamental property, though easier to determine. The following is a brief outline of the method<sup>1</sup>. A dumb-bell shaped test-piece (see Figure 4) having a long straight, central portion, uniform in width, was cut from the  $\frac{3}{16}$  inch thick moulded sheet, grips being arranged to conform automatically to the shoulders of the widened ends. Load was applied at such a rate that the samples broke in about two minutes. An extensometer connected between small pins P, P was used to magnify the elongation and operate a recording mechanism when required. By this means the elongation of the test-piece was measured at various pre-arranged loads and stress-strain curves were plotted from these observations.

Typical stress-strain curves are shown in Figures 5 and 6 and it is seen that the curves are comparatively straight up to about two-thirds of the breaking load. Increase of load beyond this point causes a rapid increase in elongation until, near the breaking point, the slope of the curve is more than ten times as great as initially.

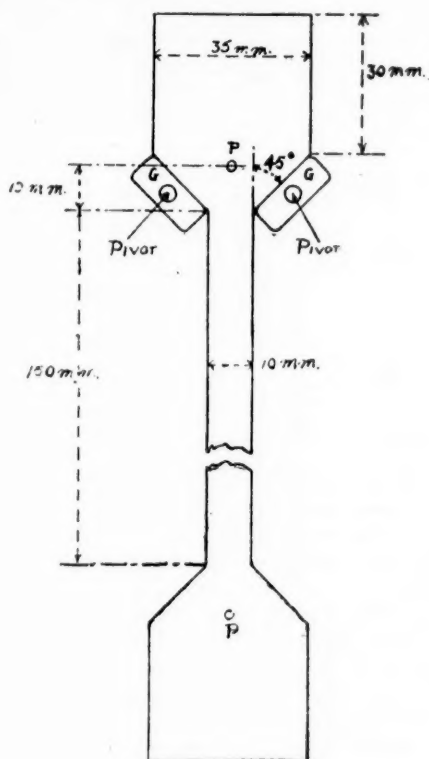
(iii) Young's Modulus.—Since the stress-strain curve of hard rubber was moderately straight over the initial portion, an average value of Young's modulus was calculated. The curvature, though small, was appreciable, and there was some difficulty in determining the zero reading, so more regular values were obtained by calculating the modulus from the increase in elongation on increasing the load from 100 to 400 kg. per sq. cm., i.e., from the formula:

$$\frac{300 \text{ kg. per sq. cm.} \times \text{initial length}}{\text{increase in length from 100 to 400 kg. per sq. cm.}}$$

(iv) Resilient Energy.—The "resilient energy", or work done in stretching unit volume of a test-piece to its breaking point, calculated as the area between the stress-strain curve and the strain axis, is often measured in connection with

\* Reprinted from the *Journal of Rubber Research*, Vol. 15, No. 7, pages 127-153, July 1946. For Part XV, Section (1), see *Journal of Rubber Research*, Vol. 14, No. 11, pages 165-172, November 1915, and *RUBBER CHEMISTRY AND TECHNOLOGY*, Vol. 19, No. 3, pages 760-772, July 1946.

the reinforcement of soft vulcanized rubber. The term is used here because it is common in rubber technology, but the use of the word "resilient" should not be taken to imply that the energy expended in stretching the test-piece is stored elastically and returnable on contraction. The resilient energy was calculated from the stress-strain curves because it might prove to have a connection with impact strength, although it was recognized that the two tests differ both in type of stress and in the time factor.



G.G. Self adjusting grips

Fig. 4.  
Form of dumbbell test-piece  
for tensile strength test.

#### (b) Results

The results are shown in Table 5. Each figure in columns 3 and 4 is the mean of six readings. The maximum variation from the mean in any set was 0.5 to 1.5 per cent in tensile strength, and 5 to 15 per cent in breaking elongation, according to the mixing and vulcanization time.

Tensile strength, breaking elongation, Young's modulus, and resilient energy are plotted against vulcanization period in Figures 7, 8, 9, and 10, respectively.



Figures 5 and 6 show stress-strain curves (average values for groups of similar specimens) for three vulcanization times with mixing B, and for samples A, B, and C vulcanized for 5 hours, respectively.

TABLE 5  
TENSILE PROPERTIES

Mixing and nominal rubber-sulfur ratio	Vulcanization (hrs. at 155° C)	Tensile strength (kg. per sq. cm.)	Breaking elongation (%)	Young's modulus, (kg. per sq. cm.)	Resilient energy (kg.-cm. per cc.)
A 65/35	3	742	5.00	24600	26.6
	3.75	771	4.83	26100	25.6
	5	793	6.17	25000	35.3
	7	813	6.29	25600	37.0
	10.5	782	7.00	24600	40.8
B 68/32	3	716	5.01	24800	25.4
	3.75	753	5.46	24500	29.3
	5	755	6.12	24000	33.6
	7	767	5.93	24000	32.2
	10.5	753	6.67	23900	37.0
C 72/28	3	633	4.68	22300	20.9
	3.75	712	5.53	24300	28.3
	5	692	5.80	22100	29.1
	7	721	6.04	22800	31.9
	10.5	694	6.20	22200	31.5

### (c) Discussion of Results

#### Influence of Vulcanization Time

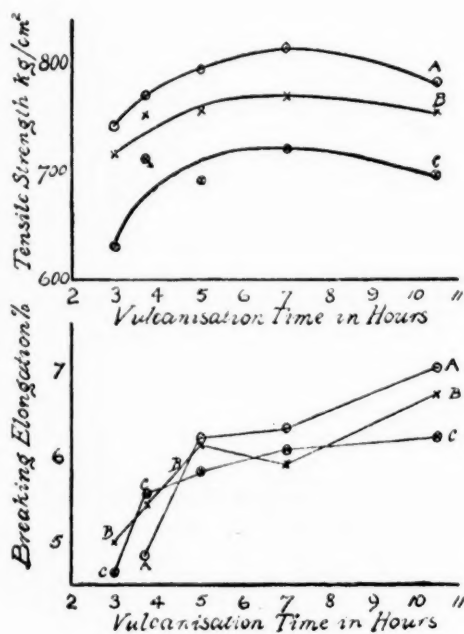
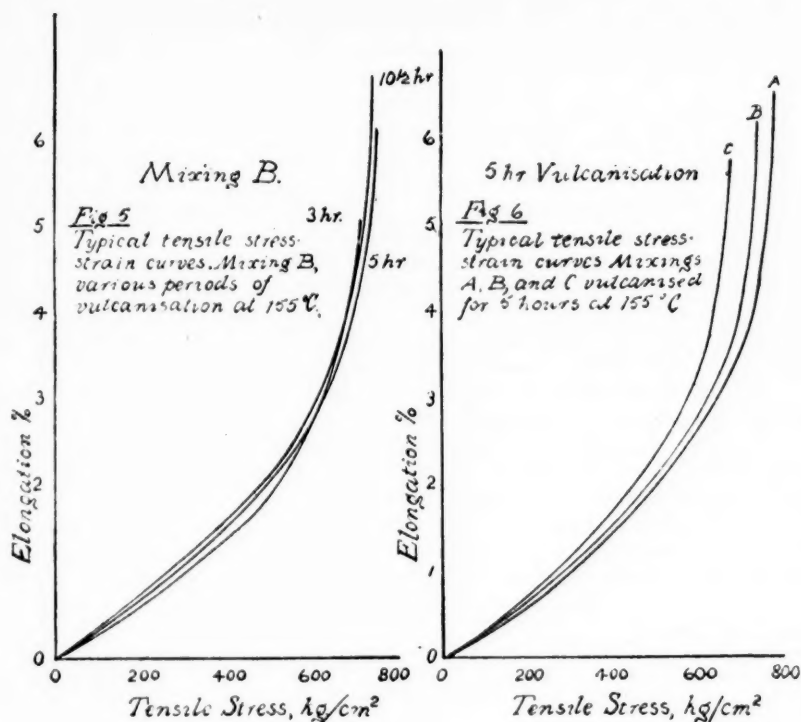
(i) In all three mixings tensile strength has a maximum value at about 7 hours' vulcanization, but the maximum is not very sharp. The shape of curve is generally in agreement with the results of Glancy<sup>2</sup>, Glancy, Wright, and Oon<sup>3</sup> and Marchandise<sup>4</sup>.

In all mixings, breaking elongation increases with vulcanization time from 3 to 10.5 hours, but most rapidly from 3 to 5 hours. This increase is not shown by the results of Glancy, Wright and Oon and of Marchandise. It was found in most cases that the specimen was drawn out to a constriction near the breaking point, so that the elongation was partly due to general elongation of the whole specimen and partly to local permanent deformation. The percentage elongation is, therefore, not a simple property, the extent to which the drawing out of the center portion contributes to the result being uncertain and dependent on the length of test-piece.

(ii) The set of superposed stress-strain curves for the three samples of B shown in Figure 5 is typical of the three mixings. There is a slight displacement of one curve due, probably, to a zero error and some variations in the rapidly yielding part of the curve, but on the whole there is no systematic and marked variation of the curve with vulcanization time as there is with soft rubber.

(iii) Young's modulus is influenced very little by vulcanization time, there being a slight continuous decrease of a few per cent.

(iv) Resilient energy increases with vulcanization time, being largely dependent on the breaking elongation, but appears to be approaching a limit or maximum shortly after 10.5 hours, the increase occurring mainly between 3 and 5 hours.



### Influence of Rubber-Sulfur Ratio.

(i) The higher the percentage of sulfur, the greater is the tensile strength for a given vulcanization time, but the variation at the optimum vulcanization time is only 12 per cent, the difference between A and B being a little less than between B and C. This result is in accordance with the following previous observations. Glancy<sup>2</sup> found an increase in strength with sulfur content up to 40 per cent, after which there was a decline. Marchandise<sup>4</sup> found an improvement from 20 to 31 per cent sulfur. Ramondt<sup>5</sup> found an optimum at 41 per cent, but the variation was slight, from 33 to 47.5 per cent.

Breaking elongation results are rather irregular, but there appears to be a slight increase generally with sulfur content for a given time of vulcanization of 5 hours or more. Glancy<sup>2</sup> and Marchandise<sup>4</sup> record slight variation in the opposite direction, while Ramondt's results, which were rather erratic, show no consistent variation with rubber-sulfur ratio.

(ii) The stress-strain curves for A, B, and C (5 hours) in Figure 6 show a definite separation and a general improvement with increasing sulfur content.

(iii) Young's modulus increases with sulfur content, A, B, and C being separated by steps of about 5 per cent. This is in agreement with Ramondt<sup>5</sup>, who found a steady increase from 23 to 47.5 per cent sulfur.

(iv) Resilient energy generally increases with sulfur content for a given vulcanization time, as would be expected from the results on the contributory properties of tensile strength, elongation, and Young's modulus.

### Absolute Values

The tensile strengths observed are in general rather higher than those reported by other observers, *e.g.*, Glancy<sup>2</sup>, Glancy, Wright, and Oon<sup>3</sup>, and Marchandise<sup>4</sup>.

The breaking elongation obtained by Glancy was of the same order of magnitude, but the values obtained by Marchandise were considerably higher. In the latter case no details of test-pieces were given and the difference may have been due to the use of a short specimen (*see* Influence of Vulcanization Time (i) above).

Ramondt<sup>5</sup>, who used Madagascar rubber, obtained considerably lower values of Young's modulus.

## 5. CROSS-BREAKING STRENGTH AND DEFLECTION

### (a) Method of Test

Cross-breaking strength was determined by the method of three-point loading<sup>6</sup>, in which a sample of rectangular section is supported on two parallel rounded knife-edges and the load is applied centrally by another such knife-edge. The following are the main particulars.

Length of test-piece	7.5 cm.
Distance between outer knife-edges	5.08 cm.
*Radius of curvature of outer knife-edges	1/16 in.
*Radius of curvature of center knife-edge	1/8 in.
Width of test-piece	2.5 cm.
Thickness of test-piece (= thickness of sheet) about	0.5 cm.
Rate of loading to break in about as determined by preliminary tests	1 min.

\* As recommended by the British Electrical & Allied Industries Research Association.

If the usual assumptions involved in the theory of bending tests held up to the breaking point, *i.e.*, that the modulus of elasticity is constant over the whole

Young's Modulus,  $\text{kg/cm}^2 \times 10^3$

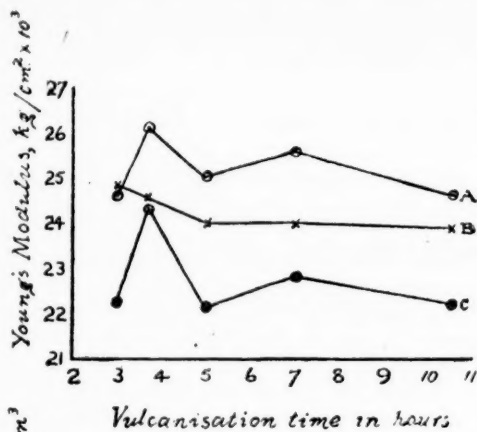


Fig. 9

Influence of vulcanisation time on Young's modulus determined under tensile stress of materials A, B, and C

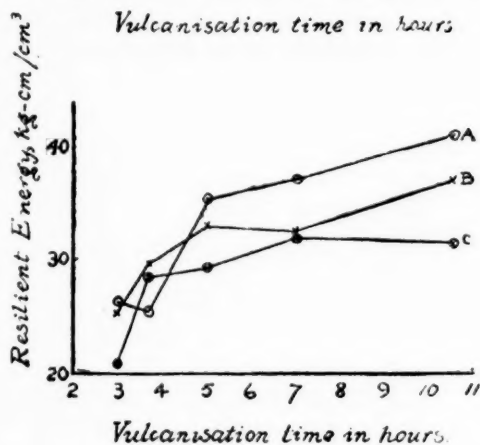


Fig. 10

Influence of vulcanisation time on resilient energy in the tensile strength test of materials A, B, and C.

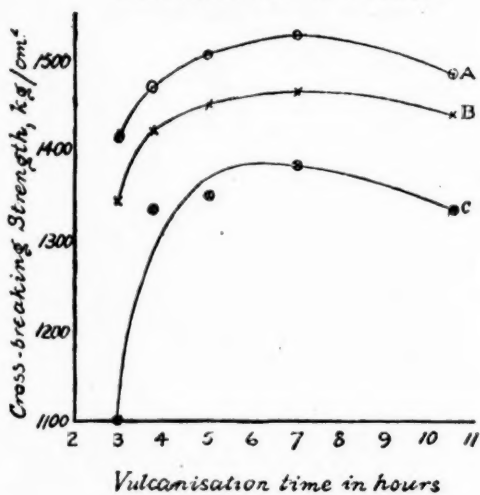


Fig. 11

Influence of vulcanisation time on cross-breaking strength of materials A, B, and C

range of tension and compression, and that the deflection of the center of the specimen is small, then the tensile strength and breaking elongation of the material could be calculated from the following formulas:

$$\text{Tensile strength} = \frac{3}{2} \cdot \frac{WL}{BD^2} \quad \text{Breaking elongation} = \frac{6 Dy}{L^2} \times 100\%$$

where  $W$  = breaking load,  $y$  = deflection of center of specimen at break,  $L$  = distance between the outer knife-edges,  $B$  = width of test-piece,  $D$  = thickness of test-piece.

The above assumptions are known to be untrue for the hard rubbers examined here (see stress-strain curves in previous section), so the values of "tensile strength" and "elongation" determined in this way differ in absolute value from those determined directly by tensile tests. However, the values obtained are independent of dimensions of test-piece over a wide range, so it is convenient to tabulate results in terms of "apparent tensile strength" and "apparent breaking elongation" and treat them as specific properties of the material. "Apparent tensile strength" is the quantity usually termed "cross-breaking strength".

TABLE 6  
CROSS-BREAKING STRENGTH AND ELONGATION

Mixing and nominal rubber-sulfur ratio	Vulcanization (hours at 155° C)	Apparent tensile strength (kg. per sq. cm.)	Apparent breaking elongation (%)	CBS TS
A 65/35	3	1410	14.1	1.90
	3.75	1470	10.4	1.91
	5	1505	11.2	1.90
	7	1530	10.4	1.88
	10.5	1480	11.0	1.89
B 68/32	3	1345	16.2	1.88
	3.75	1420	12.3	1.89
	5	1450	11.3	1.92
	7	1460	11.5	1.90
	10.5	1440	11.9	1.91
C 72/28	3	1100*	29.7*	1.74
	3.75	1335	15.2	1.87
	5	1350	14.1	1.95
	7	1380	13.4	1.91
	10.5	1335	13.3	1.93

\* No sharp break; cracked gradually underneath.

#### (b) Results

The results are shown in Table 6 and plotted in Figures 11 and 12. Each figure is the mean of six values, of which the maximum variation from the mean was 1-2 per cent in cross-breaking strength and 10-15 per cent in elongation.

The last column shows the ratio:  $\frac{\text{Cross-breaking strength (CBS)}}{\text{Tensile strength (TS)}}$

#### (c) Discussion of Results

##### Influence of Vulcanization Time

In all mixings cross-breaking strength has a maximum value at about 7 hours' vulcanization, but the maximum is not sharp. Apart from C, 3 hours, the variation with vulcanization is less than 4 per cent from 3.75 to 10.5 hours.

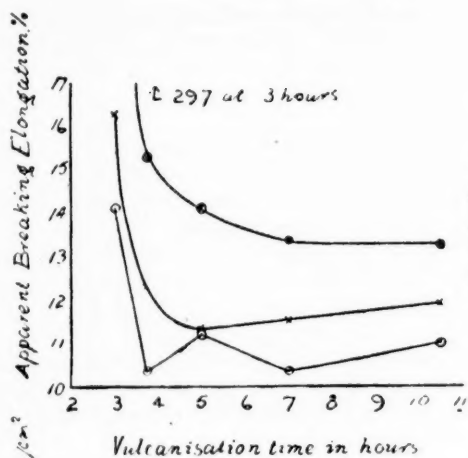


Fig. 12

Influence of vulcanisation time on apparent breaking elongation in the cross-breaking strength of materials A, B, and C

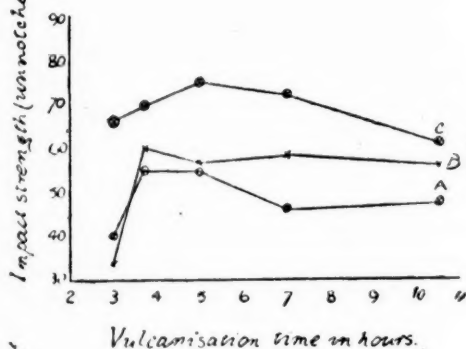


Fig. 13

Influence of vulcanisation time on impact strength (unnotched test pieces) of materials A, B, and C

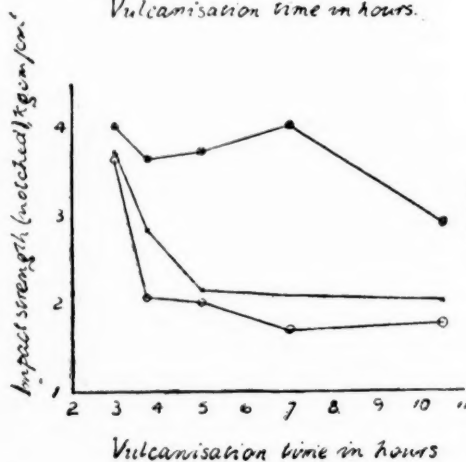


Fig. 14

Influence of vulcanisation time on impact strength (notched test pieces) of materials A, B, and C



The "apparent breaking elongation", which is proportional to the deflection at the center of the bar, decreases rapidly with increasing vulcanization time, especially in mixing C. With A and B there is a tendency towards a minimum at about 5 hours, and the variation from 3.75 to 10.5 hours is less than 10 per cent.

As in the tensile test, there was always a marked permanent deformation at the center of the test-piece, in this case on the underside. This, no doubt, had a great influence on the deflection at the center and so on the "apparent breaking elongation". In this connection it is seen that breaking elongation in the tensile test and "apparent breaking elongation" in the cross-breaking test are altered in opposite directions by vulcanization time.

#### Influence of Rubber-Sulfur Ratio

Cross-breaking strength increases with increasing sulfur content, but the difference is only 10 per cent between the extreme cases at the optimum vulcanization time. The least vulcanized sample of the low-sulfur mixing, however (C, 3 hours), is definitely deficient in strength.

Unlike the elongation in the tensile test, the "apparent breaking elongation" decreases with increasing sulfur content. The decrease is very marked between 28 and 32 per cent sulfur at 3 hours' vulcanization time, but the former sample is definitely undervulcanized and cracks on the underside instead of breaking sharply.

The practical value of a high breaking elongation is very difficult to assess. Other things being equal, a high value is desirable, but it is always observed that those materials (low sulfur and short vulcanization) with high elongation tend to have high permanent set after rupture also and would, no doubt, be permanently distorted or fatigued by stresses appreciably less than the breaking stress. This point will recur in connection with impact testing.

#### Absolute Values of Cross-Breaking Strength

The values obtained here are much higher than those given by other observers for hard rubbers stated to be made from only rubber and sulfur<sup>7</sup>; but values varying up to 2180 kg. per sq. cm. have been given for materials described as of good quality.

#### Ratio of Cross-Breaking Strength to Tensile Strength

It will be seen that there is great similarity in the effects of rubber-sulfur ratio and vulcanization time on tensile and cross-breaking strengths, as is indicated by the approximate constancy of ratio between the two strengths, the ratio varying much less than either the tensile or cross-breaking strength.

### 6. IMPACT STRENGTH

#### (a) *Methods of Test*

Impact strength is defined in this report in terms of the kinetic energy required in a striker just to break a strip of the material by a high-speed blow delivered midway between the knife-edges which support the specimen, *i.e.*, by the three-point loading method as in the cross-breaking strength test. The test, therefore, differs somewhat from the pendulum test in which a definite blow is applied, more than sufficient to break the specimen, and the energy absorbed in the fracture is calculated by subtraction of the residual from the initial energy of the pendulum, with or without a correction for the kinetic

energy of flying fragments of the broken material. The following is a brief description of the essential features of the apparatus developed by the Research Association of British Rubber Manufacturers<sup>3</sup>.

A knife-edge is weighted and allowed to fall vertically between guides with a known velocity (*i.e.*, from a known height) on to the center of a straight strip of the material supported edgewise on two parallel and horizontal knife edges. The knife-edge dimensions and spacing are the same as in the cross-breaking strength test. Two types of test-piece are adopted, namely notched and unnotched, and the apparatus may be used by three different methods, as described below, to measure the energy required for fracture. In the notched test-piece, the notch is on the underside and midway between the supporting knife-edges so that the specimen is struck immediately above the notch. The energy required for fracture is expressed in kg. per cm. per sq. cm. of cross-sectional area at the fractured section.

The following are the dimensions of the test-pieces.

(a) Plain test-piece: length, 75 mm.; depth, 12.7 mm.; width about 5 mm. = thickness of sheet.

(b) Notched test-piece: length, 75 mm.; total depth, 19 mm.; width about 5 mm. = thickness of sheet.

A vertical notch 6.3 mm. deep and rounded to 1.6 mm. radius is made across the center of the under surface of the test-piece by drilling a hole (52 gauge) through the test-piece perpendicular to the side face and joining the hole to the nearest edge by a saw cut. The remaining depth is therefore 12.7 mm., equal to the total depth of the unnotched test-piece, so that the cross-sectional areas subjected to maximum stress are the same in both notched and unnotched test-pieces.

#### Method 1

In the first method of test, the criterion of the impact energy required for fracture (following the practice adopted in some experimental work by the British Electrical and Allied Industries Research Association) is taken to be that which breaks and fails to break equal numbers of test-pieces if a large number are subjected to this blow, each test-piece being hit once only. The procedure is as follows. Thirty test-pieces of each material are prepared and divided into sets of six each, and each set is given a different impact blow per unit area of cross-section, the velocity of impact being fixed. On plotting percentage of breaks against energy of flow, the blow which would have broken half the test-pieces subjected to that blow can be interpolated.

The velocity of impact adopted is: (a) Plain test-piece, 300 cm. per sec. (corresponding to fall of 45.9 cm.); (b) Notched test-piece, 200 cm. per sec. (corresponding to fall of 20.4 cm.).

This difference of velocity is necessary with unloaded hard rubbers owing to the great difference in blow required by the two types of test-piece and the limitations of load in the apparatus as constructed.

The disadvantages of Method 1 are that (a) a large number of test-pieces is necessary, requiring considerable material and time in preparation, and (b) the percentage of breaks in a set of six is greatly affected by any abnormality in a single specimen, thus introducing uncertainty into the interpolation.

#### Method 2

Partly to economize in test-pieces, a modified method has been devised, in which each test-piece is subjected to a series of blows of rapidly increasing

magnitude until breakage occurs. This involves a departure from standard practice in which each specimen is struck once only, but it does not appear to be an objectionable change, for if the strength of a material is greatly affected by a few previous blows, only one or two of which are comparable with the breaking blow, the information may be quite as valuable as if only the simpler property were involved.

In the case of unnotched samples a fixed weight is released successively from heights of 10, 20, 30, 40 cm., and so on until breakage occurs, the load being selected by preliminary tests so that, on the average, half the specimens are fractured by a fall from a height of 40 cm. The impact strength of each sample is regarded as the product of the falling weight per unit area of cross-section and the mean of the height which causes the break and the preceding height of release. The impact strength of the material is taken as the mean of the impact strengths, so defined, of the individual samples.

The same method is used for notched samples except that the series of heights of fall is 5, 10, 15, 20, 25, etc., cm., the load being selected so that, on the average, half the specimens are fractured by a fall from a height of 20 cm.

Generally, with this method a consistent result can be obtained with as few as 12 test-pieces, since every specimen is broken and the strength of each test-piece is known to within narrower limits than with the first method. Exact agreement between the two methods is not necessarily to be expected, since the fatigue factor enters into the second method.

### Method 3

To emphasize the fatigue factor still more, the second method has been modified as follows, and applied to unnotched test-pieces of some of the materials. Each of the series of increasing blows, obtained by successively increasing the height of fall in the stages 10, 20, 30, 40 cm. and so on, was repeated to a total of six times before applying the next of the series, the load being the same as in Method 2 and the impact strength being calculated in the same way. Method 2, besides being economical and convenient in operation has been found to give more regular results than Method 1 and has been adopted as the usual test method. However, results which have been obtained by Methods 1 and 3 will be recorded since there are significant differences between them.

The results of the tests are shown in Table 7 and are plotted against vulcanization time in Figures 13 and 14.

### (b) Results

During the testing of unnotched test-pieces it was observed that, although materials from mixing C had higher impact strength than those with a higher sulfur content, blows which just failed to break the former materials produced a large permanent deformation. This raised the question whether C should in practice be credited with the high impact strength shown in Table 7, since a severe distortion might be as serious as breakage. Although no definite investigation of this point was made, a few measurements were taken as a preliminary step towards a proper study of the phenomenon and its relation to the question of fatigue.

Some months after the impact tests by Method 1 had been made, a number of test-pieces which had withstood the blows applied were examined for permanent distortion by measuring the displacement of the center of the test-piece. In the case of Method 2, where every test-piece is broken, the measurement was

made during impact testing after each blow. No permanent deformation was detectable in notched test-pieces.

The results are shown in Table 8 in two forms. The "permanent distortion" is the measured distortion due to a blow which would break half the test-pieces. It was found also in examining the results that deformation began to appear at a fairly definite blow and to be roughly proportional to the excess above that blow. This limiting blow is shown in the columns headed "yield point".

TABLE 7  
IMPACT STRENGTH

Mixing and nominal rubber-sulfur ratio	Vulcanization (hours at 155° C)	Impact strength (unnotched), kg.-cm. per sq. cm. by method			Impact strength (notched) (kg.-cm. per sq. cm.) by method	
		1	2	3	1	2
A 65/35	3	33.3	40	32.5	3.32	3.6
	3.75	56.3	55.5	—	2.86	2.05
	5	56.4	55	38.4	2.28	2.0
	7	52.2	46	—	5.80	1.7
	10.5	42.0	46.5	24	2.04	1.75
B 68/32	3	66.0	33	24	3.88	3.7
	3.75	66.0	60	—	2.36	2.8
	5	57.9	56.5	41.7	3.4	2.1
	7	53.7	59	—	2.70	2.05
	10.5	33.7	56	40	1.98	2.0
C 72/28	3	62.2	66	42.5	5.22	4.0*
	3.75	85.5	70	—	6.58	3.6
	5	93.9	75	48.5	4.28	3.7
	7	83.2	72	—	7.06	4.0
	10.5	83.0	61	43	2.5-3	2.9

\* Only 6 samples tested.

### (c) Discussion of Results

It appears to be the opinion of those experienced in the testing of insulating materials that impact strength is one of the mechanical properties which it is most difficult to assess by laboratory tests. The strength appears to be very sensitive to a number of untraced variables in the manufacture of the material and in the preparation of test-pieces; for it is usually found that there is considerable variation even between specimens taken from a single sheet and still more between sheets or mouldings of nominally the same composition prepared at different times. For example, in Table 7 there are certain irregularities (e.g. low values for A, 3 hours, and B, 10.5 hours, by Method 1, unnotched; high value 5.80 for A, 7 hours, Method 1, notched; and variation with vulcanization time of C, 3 to 10.5 hours, Method 1, notched) which are at present unexplained, since they are not due to any excessive variation among the results from which each mean value was obtained. In view of this experience both here and elsewhere, results from impact tests quoted above must be accepted with more caution than is necessary with most other properties, and confirmation will be sought by a certain amount of repetition in making up new materials for future work. For the same reason comment on the results will be confined to the outstanding relations. As already explained, Method 2 has been adopted as the principal type of test and the following discussion will refer mainly to results by this method, those obtained by Methods 1 and 3 being used to throw some light on the nature of impact fracture in hard rubber.

## (1) Comparison of Methods 1, 2, and 3

A comparison of the three methods of test is of interest, (a) in showing the effect of repeated impact, and (b) in showing to what extent the departure from the practice of striking each sample only once invalidates comparison of results by the present and previous methods.

*Influence of Vulcanization Time.*—Tables 7 and 8 show that, apart from some irregularities noted above, the three methods show no substantial differences in their assessment of the relative merits of the vulcanization times adopted. This is the case, so far as the methods were applied, with all mixings and both types of test-piece.

TABLE 8  
PERMANENT DEFORMATION OF UNNOTCHED TEST-PIECES

Mixing and nominal rubber- sulfur ratio	Vulcanization (hours at 155° C)	Method 1		Method 2	
		Permanent distortion (mm.)	Yield point (kg.-cm. per sq. cm.)	Permanent distortion (mm.)	Yield point (kg.-cm. per sq. cm.)
A 65/35	3	No detectable yield		—	—
	3.75			—	—
	5			—	—
	7	—	—	—	—
B 68/32	10.5	—	—	0.00	—
	3	0.03	60	—	—
	3.75	0.03	60	—	—
	5	—	—	—	—
C 72/28	7	0.00	70	—	—
	10.5	—	—	—	—
	3	0.20	49	0.18	53
	3.75	0.17	60	0.05	64
	5	—	—	—	—
	7	0.065	72	—	—
	10.5	—	—	0.00	approx. 70

*Influence of Rubber-Sulfur Ratio.*—Methods 1 and 2 are substantially in agreement as to the absolute values of the impact strength of A and B with both notched and unnotched test-pieces. With mixing C, however, the strength is less by Method 2 than by Method 1, the differences being on the average 15 and 25 per cent with unnotched and notched specimens, respectively. Thus, by Method 2, mixing C remains superior to A and B though to a less degree. All mixings show considerable loss of strength (unnotched) on application of Method 3 instead of Method 2, the reductions being, on the average, about 32, 27, and 33 per cent for A, B, and C, respectively. Thus, although Method 2 gives a lower strength than Method 1 with mixing C, and no difference with A and B, all mixings are affected almost to the same extent by the change to Method 3.

## (2) Comparison of Notched and Unnotched Test-pieces

*Ratio of Unnotched to Notched Strength.*—It is clear that the strength of the notched test-piece is very much less than that of the unnotched in all cases; and other experiments, not recorded here, have shown that the strength of an unnotched test-piece is seriously reduced by even a small scratch on the underside. The ratio of the strengths by Method 2 is shown in Table 9.



No similar comparison of the two types of test-piece with definite rubber-sulfur hard rubbers is recorded in the literature, but Ariano<sup>9</sup> and Flight<sup>10</sup> have shown similar differences between results obtained on notched and unnotched samples of high grade materials. In the former case, the unnotched values were much nearer the notched values, i.e., lower, than in the present work. Impact strengths of unnotched samples comparable in magnitude with those of the present report, but always rather less, have been obtained on known rubber-sulfur materials by Dieterich and Gray<sup>11</sup>, Geisler<sup>12</sup>, and Schering<sup>13</sup>.

Previous determinations on notched samples are difficult to compare with the present results, on account of the great influence of notch size. Moreover, most of the results available only apply to materials stated to be of very high

TABLE 9  
RATIO OF UNNOTCHED TO NOTCHED IMPACT STRENGTH

Mixing and nominal rubber- sulfur ratio	Vulcanization (hours at 155° C)	Ratio unnotched/notched
A 65/35	3	11.1
	3.75	27.0
	5	27.5
	7	27.1
	10.5	26.6
B 68/32	3	8.9
	3.75	21.4
	5	26.8
	7	28.9
	10.5	28.0
C 72/28	3	16.5
	3.75	19.4
	5	20.3
	7	18.0
	10.5	21.0

grade but of indefinite composition. This is true of the results of Ariano<sup>9</sup>, and Flight<sup>10</sup>, which are comparable in magnitude with the results of Table 7. The results of Marchandise<sup>4</sup>, however with a 1-mm. square notch, are unaccountably high, varying from 16 to 45 kg.-cm. per sq. cm. according to mixing and vulcanization time. In case this was due to the form of notch, some material (A; 10.5 hours) was tested with both R.A.B.R.M. and Marchandise's test-piece (the latter did not give details of supports or striker) with the following results:—R.A.B.R.M. test-piece, 1.75 kg.-cm. per sq. cm.; Marchandise test-piece, 3.28 kg.-cm. per sq. cm.

The difference in notch is, therefore, not sufficient to account for the ratio of about 9 to 1 between Marchandise and R.A.B.R.M. results, although the procedure of Marchandise was very similar to that of the R.A.B.R.M., a 500-gram weight being allowed to fall on the sample from heights of 5, 10, 15, 20 cm., and so on in succession.

*Influence of Vulcanization Time.*—It seems that to some extent different physical properties are involved in impact strength of notched and unnotched test-pieces, for it is differently affected by vulcanization time in the two cases. Whereas unnotched test-pieces show a maximum strength at about 5 hours, there is a continuous decrease in strength of notched test-pieces with increasing vulcanization time, though this effect is not so marked with mixing C. This



difference between the two types of test-piece is shown in the low values of the ratio for 3 hours' vulcanization in Table 9, the ratio being higher and substantially independent of vulcanization time from 3.75 to 10.5 hours. In other words, the weakening effect of the notch is much less with 3 hours' vulcanization than with longer periods.

*Influence of Rubber-Sulfur Ratio.*—There is little difference between mixings A and B in the relative strengths of notched and unnotched test-pieces, but the weakening effect of the notch is much less with mixing C and less dependent on vulcanization time, as shown by the low and more nearly constant value of the ratio in Table 9. In other words the superiority of C over A and B is more marked with notched than with unnotched test-pieces.

### (3) Impact Strength and Permanent Deformation by Method 2

*Influence of Vulcanization Time.*—All mixings show a maximum strength at 3.75–7 hours' vulcanization when tested unnotched, and in this respect the results resemble those of the tensile and cross-breaking strength tests. The optimum is shown by all three methods in which the fatigue factor plays different parts (see Table 7 and Figures 13 and 14). With the notched test-piece, the strength falls rapidly on vulcanization from 3 to 5 hours and then becomes approximately steady in mixings A and B, while with mixings C there is comparatively little fall until after 7 hours. This difference in vulcanization-time/impact-strength curve with the two types of test-piece has already been discussed. The continuous fall in strength of notched test-pieces with vulcanization time is in agreement with the results of Marchandise<sup>4</sup>, who observed a decrease from 2.5 to 20 hours, but mainly before 4 hours. The permanent distortion (Table 8) corresponding to the average breaking blow decreases with vulcanization time in those cases where it has been measured and found detectable. The blow at which the distortion becomes detectable increases with vulcanization time.

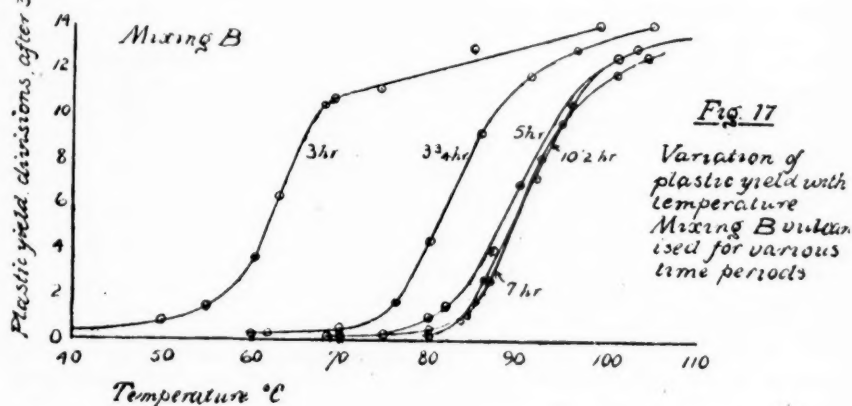
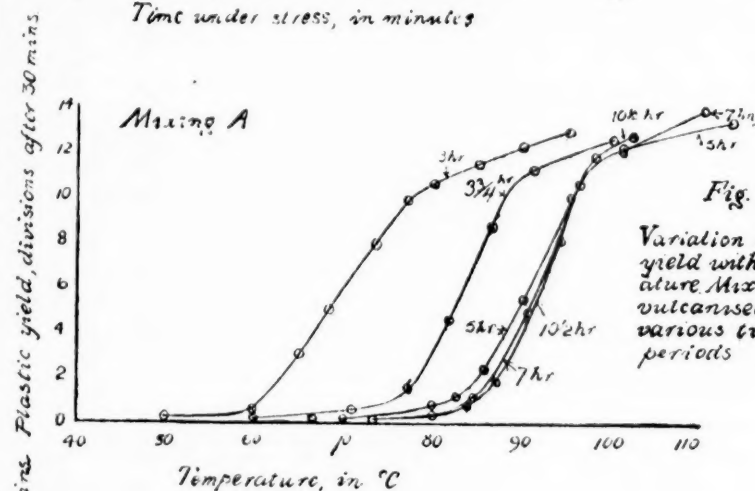
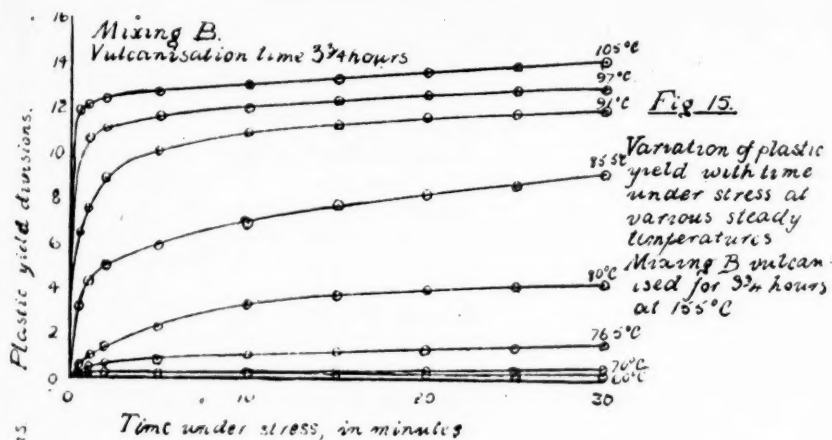
*Influence of Rubber-Sulfur Ratio.*—The low-sulfur mixing C is superior at all vulcanization times and with both types of test-piece to mixings A and B, which resemble one another closely (see Table 7 and Figures 13 and 14). The superiority is most marked with the notched test-piece except possibly at 3 hours' vulcanization when C is more closely approached in strength by mixings A and B. The greater impact strength of the low-sulfur mixing is in agreement with the results of Marchandise<sup>4</sup> in which a 74/26 mixing was greatly superior to a 69/31 mixing at all vulcanization times. These conclusions as to the relative merits of mixings A, B, and C are borne out by results with Method 3 (unnotched only) and Method 1, though those of the latter are less regular. Permanent deformation after impact corresponding to the average breaking blow is greater the lower the percentage of sulfur, though it must be remembered that the average breaking blow is greater with mixing C, so that it is not possible from the present results to compare the deformations under equal impact blows. There is insufficient evidence for a comparison of the yield points of the three mixings.

## 7. PLASTIC YIELD AND PLASTIC YIELD TEMPERATURE

### (a) Method of Test

Tests were made on all the materials to determine (a) the plastic yield under standard conditions of stress and time at various temperatures, and (b) the characteristic yield temperature as defined by the R.A.B.R.M. torsion test, of which the following is a brief outline<sup>14</sup>.

Plastic yield divisions after 30 mins



A rectangular strip is submitted to a torsional stress at a series of steady temperatures, preferably a new test-piece being used at each temperature, and the yield under this stress is measured at various times after application of the stress. On plotting yield after a given time against temperature of test, it is observed that at a fairly definite temperature the yield begins to increase very rapidly with increase in temperature, and that the temperature-yield curve in the region of rapid yield is linear. The intercept of this linear portion, when produced to cut the temperature axis, defines the R.A.B.R.M. yield temperature which, for hard rubber, is found to be independent of test-piece dimensions and the magnitude of the torque, but dependent on the time of application of the torque.

The following conditions of test have been adopted: length of test-piece between grips, 75 mm.; width of test-piece, 15 mm.; thickness of test-piece, 5 mm.; couple applied, 75 g.-cm.; duration of stress, 30 min.

In cases where the deflection under standard torque would be greater than about 10 angular degrees, a lower torque is used and correction made accordingly.

#### (b) Results

The observations of yield (corrected to standard dimensions and torque, as mentioned above) are given in Table 10, and a typical set of time-yield curves for various temperatures is shown in Figure 15.

The yield after 30 minutes at various temperatures and the yield temperature, as defined above, were obtained from smooth temperature-yield curves and are set out in Table 11. The temperature-yield curves are shown in Figures 16, 17, and 18.

To ensure that the practical value of the various materials was not likely to be misjudged seriously by using such a short period of stress as 30 minutes, three selected samples were tested also for 24 hours at one temperature (80° C). The time-yield curves are given in Figure 19. The samples tested were of mixing B vulcanized for 3, 5, and 10.5 hours.

#### (c) Discussion of Results

##### (1) Relation Between Time and Yield at Various Temperatures

It can be seen from Figure 15, and from similar sets of curves which could be drawn from the data in Table 10 that at comparatively low temperatures the materials yields slightly during the first few minutes, after which it approaches asymptotically a practically constant low value. At intermediate temperatures the rate of yield increases rapidly with temperature, but the yield continues at a decreasing rate with time during the whole of the 30 minutes. At higher temperatures the rate of yield increases still further, as also does the rate of approach to an asymptote. This asymptote, however, is not quite horizontal, the curves indicating a continuous though slow yield up to the end of the 30-minute period in all cases.

Previous work at the R.A.B.R.M. has shown that the material behaves approximately as if its structure were complex, consisting of a rigid phase which is dominant at low temperatures but flows at an increasing rate, *i.e.*, with decreasing viscosity, with increasing temperature, leaving the mechanical properties at the highest temperatures dominated by a much more flexible but nearly elastic phase. Apart from the actual values of the yield and the temperatures at which yield occurs, there is no very marked difference in the general character of the curves for all the mixings and vulcanization times. The 24-hour time-yield curves at 80° C also have the same general character.

TABLE 10

RELATION BETWEEN TIME AND YIELD AT VARIOUS TEMPERATURES  
MIXINGS (R/S), VULCANIZED AT 155° C

Time of vulcaniza- tion (hrs.)	Temp. of test (° C)	Deflection (in divisions) after time (in minutes) of								
		0.5	1	2	5	10	15	20	25	30
(A) Rubber/sulfur 65/35										
3	50	0.1	0.25	—	0.3	0.35	0.35	0.35	0.35	0.35
	60	0.25	0.3	0.3	0.35	0.4	0.4	0.5	0.5	0.5
	65	0.55	0.7	1.1	1.75	2.1	2.35	2.6	2.8	3.0
	69	1.1	1.8	2.05	2.75	3.25	4.05	4.55	4.8	4.9
	73	2.4	3.1	4.1	5.45	6.3	6.8	7.1	7.45	7.8
	76	3.6	4.6	5.3	6.3	7.8	8.55	9.3	9.55	9.8
	80	6.65	7.7	8.4	9.15	—	9.85	10.05	10.4	10.6
	85	7.3	9.3	9.7	10.2	10.55	10.9	11.05	11.15	11.3
	90	9.15	9.7	10.05	10.6	11.1	11.65	11.85	12.0	12.2
	95	10.4	10.65	11.3	11.8	12.5	12.65	12.8	12.9	12.9
3.75	60	0.05	0.05	0.05	0.10	0.10	0.10	0.10	0.15	0.15
	71	0.1	0.15	0.15	0.3	0.35	0.35	0.35	0.40	0.45
	77	0.2	0.3	0.35	0.6	0.8	1.05	1.2	1.35	1.4
	82	0.75	1.15	1.35	2.0	2.7	3.3	3.8	4.1	4.45
	87	2.95	4.05	5.3	6.75	7.5	7.85	8.2	8.6	8.8
	91	5.25	6.8	8.0	9.1	9.45	10.0	10.8	11.05	11.25
	100	9.2	9.9	10.65	11.15	11.65	12.15	12.25	12.5	12.5
5	70	0.05	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2
	80	0.25	0.3	0.3	0.4	0.4	0.4	0.5	0.6	0.6
	82.5	0.1	0.2	0.25	0.35	0.55	0.75	0.85	1.0	1.05
	86	0.45	0.6	0.75	1.05	1.35	1.6	1.85	2.05	2.3
	90	0.65	0.85	1.10	2.0	3.3	3.85	4.4	4.9	5.5
	96	2.0	2.45	3.35	4.05	6.15	8.9	9.1	9.6	10.25
(Temperature fluctuated)										
	101	8.75	9.25	9.85	10.3	11.15	11.4	11.65	11.75	12.0
	108.5	10.1	10.7	10.7	10.9	11.9	12.45	12.85	12.95	13.1
7	73	—	0.05	0.05	0.05	0.1	0.1	0.2	0.2	0.2
	80	0.05	0.1	0.1	0.1	0.15	0.15	0.25	0.3	0.3
	84.5	0.2	0.25	0.25	0.35	0.55	0.85	0.95	1.05	1.15
	90.5	0.4	0.65	1.0	1.8	2.65	3.4	3.9	4.4	4.8
	95.5	2.5	3.35	—	6.55	7.85	8.95	9.65	9.8	9.9
	101	6.4	7.4	8.8	10.2	10.65	11.1	11.25	11.6	12.05
	105.5	9.5	10.5	10.95	11.65	12.0	12.4	13.45	13.8	13.9
	110	10.3	10.9	11.35	11.95	12.75	13.45	14.0	14.5	15.2
10.5	67	0.05	0.05	0.05	0.05	0.15	0.15	0.15	0.15	0.15
	75	0.15	0.2	0.2	0.25	0.3	0.4	0.4	0.45	0.45
	84	0.05	0.15	0.2	0.3	0.5	0.75	0.9	0.95	0.95
	87	0.2	0.25	0.4	0.55	0.95	1.25	1.3	1.5	1.7
	94	1.4	2.05	2.8	4.25	5.45	6.4	7.0	7.45	8.0
	98	4.5	5.1	7.0	8.25	9.6	10.0	10.4	12.0	11.65
	102	4.55	6.35	7.6	9.4	11.2	11.8	11.95	12.45	12.7
	107	10.4	11.25	11.65	11.9	13.0	13.65	14.0	14.15	14.25

TABLE 10—Continued

Time of vulcaniza- tion (hrs.)	Temp. of test (° C)	Deflection (in divisions) after time (in minutes) of								
		0.5	1	2	5	10	15	20	25	30
(B) Rubber/sulfur (68/32)										
3	40	0.05	0.05	—	0.15	0.15	0.15	0.2	—	0.3
	50	0.15	0.30	0.3	0.3	0.35	0.45	0.5	0.5	0.5
	55	—	0.4	0.45	0.65	—	1.0	1.1	1.3	1.45
	60.5	0.5	0.9	1.0	1.5	2.05	2.3	2.95	3.4	3.45
	63	1.6	1.95	2.45	3.3	4.2	—	5.7	6.1	6.45
	68	3.4	4.5	5.7	7.3	8.4	9.5	10.0	10.35	10.45
	69	3.75	5.0	6.6	8.4	9.5	10.0	10.5	10.6	10.75
	74.5	6.6	7.7	8.9	9.45	9.9	10.3	10.6	11.0	11.15
	85	10.6	11.0	11.45	11.6	11.9	12.0	12.3	12.7	12.85
98	10.5	11.4	12.05	12.5	13.15	13.4	13.6	13.8	14.0	
3.75	60	0.1	0.1	0.2	0.2	0.2	0.25	0.25	0.25	0.25
	70	0.1	0.2	0.25	0.25	0.3	0.35	0.4	0.45	0.5
	76.5	—	0.5	0.75	1.15	1.3	1.4	1.45	1.5	1.6
	80	0.6	1.05	1.5	2.25	3.3	3.75	4.0	4.2	4.35
	85.5	3.15	4.4	5.0	5.85	6.8	7.8	8.2	8.55	9.05
	91	6.45	7.6	8.9	10.05	10.9	11.25	11.6	11.7	11.8
	97	—	10.75	11.1	11.6	11.95	12.35	12.6	12.7	12.8
	105	11.85	12.05	12.3	12.65	13.0	13.2	13.6	13.8	14.05
5	62	0.1	0.2	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	70	0.1	0.2	0.25	0.25	0.25	0.25	0.25	0.3	0.3
	80	0.25	0.3	0.35	0.55	0.65	0.75	0.8	0.9	0.9
	82.5	0.25	0.3	0.4	0.75	0.95	1.05	1.15	1.2	1.3
	87.5	0.55	0.7	1.0	1.6	2.4	3.05	3.5	3.8	4.15
	90	1.5	2.1	2.75	4.15	5.1	5.7	6.4	6.9	7.45
	95.5	2.7	5.6	6.9	7.85	8.7	9.6	10.0	10.35	10.45
	100.5	8.65	9.7	10.3	10.55	11.1	11.6	12.05	12.4	12.5
	107	10.1	10.35	10.45	10.9	11.4	11.75	12.35	12.35	12.45
	111	11.05	11.4	11.4	11.6	12.1	12.65	13.0	13.35	13.7
	7	75	0.05	0.2	0.3	0.3	0.3	0.3	0.3	0.35
80		0.1	0.1	0.1	0.2	0.25	0.3	0.35	0.45	0.5
84.5		0.2	0.25	0.25	0.35	0.55	0.85	0.95	1.05	1.15
87		0.45	0.5	0.55	0.9	1.45	1.7	2.0	2.4	2.7
92.5		1.7	2.3	3.05	4.3	5.75	6.6	7.0	7.7	8.2
94.5		—	4.05	5.25	7.3	8.5	9.2	9.55	9.7	9.8
100.5		7.2	—	9.3	10.75	11.5	11.6	11.6	11.7	11.75
104		9.45	10.3	10.75	11.45	11.95	12.2	12.4	12.55	12.65
10.5		69	0.05	0.15	0.15	0.2	0.25	0.25	0.25	0.25
	80	0.15	0.2	0.2	0.25	0.25	0.35	0.35	0.4	0.4
	84	0.3	0.3	0.35	0.5	0.6	0.65	0.8	0.85	0.9
	86.5	0.25	0.45	0.55	0.95	1.3	1.75	2.3	2.55	2.75
	92	1.5	2.2	2.8	4.05	5.4	6.25	6.85	7.0	7.3
	97.5	7.0	7.8	8.35	9.4	10.5	10.75	11.0	11.45	11.7
	102.5	8.85	9.7	10.65	11.75	12.1	12.35	12.5	12.7	12.95

TABLE 10—Continued

Time of vulcaniza- tion (hrs.)	Temp. of test (° C)	Deflection (in divisions) after time (in minutes) of								
		0.5	1	2	5	10	15	20	25	30
(C) Rubber/sulfur 72/28										
3	41	0.2	0.25	0.3	0.3	0.4	—	0.4	—	0.45
	45	0.2	0.3	0.35	0.35	0.5	0.55	0.55	0.6	0.7
	50.5	0.25	0.4	0.5	0.9	1.5	—	1.8	2.05	2.4
	54.5	1.25	1.5	1.9	2.75	3.3	—	3.45	4.25	4.7
	59.5	3.2	3.85	5.4	7.1	8.85	10.0	10.55	11.05	11.3
	64	—	8.9	10.3	11.6	13.75	14.45	14.6	14.85	14.85
	69.5	12.2	13.0	13.75	14.65	15.15	15.3	15.4	15.8	15.8
	85	15.9	16.55	17.0	17.2	17.8	18.0	18.3	18.6	18.8
	95	16.55	16.85	17.05	17.2	18.45	19.4	19.6	19.6	19.6
3.75	56	0.15	0.2	0.2	0.35	0.4	0.4	0.4	0.45	0.45
	61.5	0.1	0.15	0.25	0.25	0.4	0.5	0.75	0.9	0.95
	65	0.35	0.45	0.6	1.15	1.45	1.65	1.9	2.05	2.2
	71	1.25	1.8	2.5	4.1	5.8	6.35	6.9	7.5	7.9
	78	5.8	7.0	8.9	11.7	12.5	13.3	13.4	13.6	13.7
	85	11.45	12.25	12.8	13.4	14.05	14.4	14.65	14.75	14.9
	92	14.05	14.4	14.6	15.4	15.5	15.6	15.85	15.85	15.9
	5	53	0.15	0.15	0.2	0.2	0.2	0.25	0.25	0.25
66.5		0.2	0.25	0.25	0.25	0.35	0.4	0.45	0.45	0.55
71		0.15	0.3	0.35	0.55	0.8	0.95	1.0	1.1	1.15
74.5		0.4	0.6	0.95	1.2	1.5	1.7	1.9	2.05	2.2
77.5		1.25	1.5	1.8	2.5	3.4	4.2	4.9	5.25	5.6
82.5		2.9	4.4	5.8	7.8	8.7	9.5	10.05	10.65	11.05
85		7.5	8.7	9.2	10.6	11.6	11.8	12.15	12.15	12.15
90		9.0	10.8	11.8	12.7	13.5	13.8	13.9	13.9	14.05
95		12.15	12.65	13.0	13.7	14.2	14.2	14.35	14.35	14.55
110		14.4	14.7	14.7	14.9	15.05	15.2	15.4	15.4	15.55
7	60	0.1	0.25	0.3	0.3	0.3	0.3	0.3	0.35	0.35
	69.5	0.3	0.3	0.3	0.3	0.35	0.45	0.45	0.5	0.5
	74.5	0.25	0.3	0.4	0.56	0.95	1.05	1.1	1.2	1.25
	79.5	0.6	0.75	0.85	1.55	2.05	2.55	3.1	3.35	3.65
	82	1.1	1.6	2.5	3.25	4.5	5.5	5.9	6.6	7.0
	87.5	5.1	7.1	8.6	10.4	11.1	12.1	13.0	13.15	13.25
	89.5	6.95	7.55	10.4	11.65	12.9	13.15	13.4	13.5	13.65
	95	12.25	13	13.4	13.9	14.15	14.15	14.25	14.25	14.25
	100	13.0	13.65	13.8	14	14.25	14.4	14.5	14.65	14.75
10.5	60	0.05	0.05	0.05	0.1	0.1	0.2	0.2	0.25	0.25
	70	0.1	0.2	0.2	0.25	0.3	0.45	0.45	0.45	0.5
	76	0.4	0.45	0.6	0.75	0.8	0.85	1.0	1.15	1.3
	81	0.9	1.15	1.7	2.6	3.05	3.4	3.6	4.15	4.95
	86	—	2.95	4.4	6.55	8.45	9.1	9.5	9.9	10.6
	89.5	6.2	8.05	9.6	11.3	11.95	12.45	13.15	13.3	13.4
	98	10.4	12.05	12.45	13.65	13.95	14.05	14.2	14.35	14.5
	106	13.4	13.55	13.65	14.2	14.6	14.75	14.75	14.75	14.75



TABLE 11  
YIELD AFTER 30 MINUTES' STRESS, AND YIELD TEMPERATURE

Mixing and nominal rubber-sulfur ratio	Vulcanization (hours at 155° C)	Plastic yield in degrees at							Yield temperature (° C)
		40° C	50° C	60° C	70° C	80° C	90° C	100° C	
A 65/35	3	—	0.3	0.5	5.9	10.6	12.2	13.5	60.6
	3.75	—	—	0.2	0.4	3.2	10.9	12.8	76.0
	5	—	—	0.2	0.2	0.6	5.6	11.8	83.2
	7	—	—	—	—	0.3	5.0	11.8	85.5
	10.5	—	—	—	0.2	0.3	4.5	12.2	86.0
B 68/32	3	0.3	0.5	3.6	10.8	12.1	13.3	14.3	56.5
	3.75	—	—	0.2	0.6	4.3	11.6	13.3	74.5
	5	—	—	0.2	0.3	0.9	6.4	12.4	82
	7	—	—	—	0.3	0.5	5.9	11.0	83.5
	10.5	—	—	—	0.2	0.4	5.6	12.4	83.5
B 72/28	3	0.4	2.1	11.2	15.9	17.9	19.4	21.1	50.5
	3.75	—	approx. 0.3	0.7	6.8	14.2	15.6	16.8	62.5
	5	—	—	0.3	1.0	8.6	14.1	15.0	72.7
	7	—	—	0.3	0.6	4.3	13.7	14.8	76.5
	10.5	—	—	0.3	0.5	3.9	13.5	14.6	76.7

## (2) Relation Between Temperature and Yield After 30 Minutes

It has been previously shown by the R.A.B.R.M. that if yield after a given time, *e.g.*, 30 minutes, was plotted against temperature, there was a steep linear portion joining two flatter portions. The curves obtained for the present materials (see Figures 16, 17, and 18) conform to this type, so the definition of yield temperature given above may be applied, and the values obtained are those shown in the last column of Table 11. The slope of the central linear portion of the curve is shown in Table 12.

TABLE 12  
SLOPE OF LINEAR PORTION OF TEMPERATURE-YIELD CURVE

Vulcanization (hours at 155° C)	Slope in division per ° C (30-minute stress) for mixing		
	A	B	C
3	0.63	0.95	1.28
3.75	0.79	0.83	0.97
5	0.82	0.81	1.15
7	1.00	0.92	1.25
10.5	1.03	0.87	1.15

It may be pointed out that the existence of the second flat portion of the temperature-yield curve, where the yield again becomes almost independent of temperature, is not generally known, since the usual cantilever test is not conveniently carried out at such temperatures. The present torsion test, however, enables measurements to be taken accurately in this region.

*Influence of Vulcanization Time.*—In each of the three mixings the following effects of increasing vulcanization may be observed. (1) There is no substantial change in the general shape of the temperature-yield or time-yield curve. (2) The yield at any fixed temperature decreases continuously, the decrease being rapid while combination of sulfur is proceeding rapidly and almost ceasing when combination ceases, the temperature-yield curves for the longest vulcani-

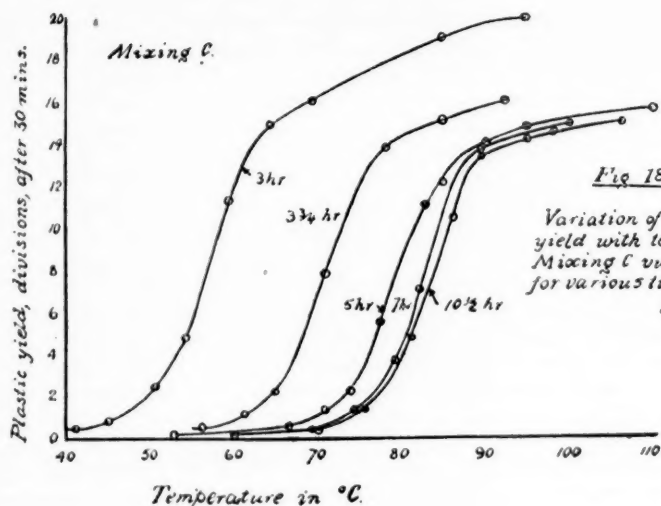


Fig. 18.

Variation of plastic yield with temperature. Mixing C. vulcanised for various time periods.

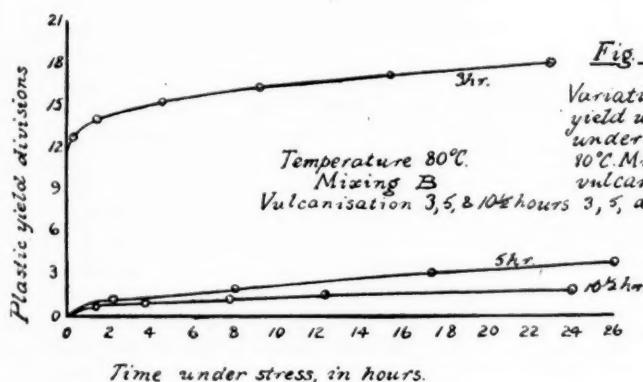


Fig. 19.

Variation of plastic yield with time under stress at 80°C. Mixing B, vulcanisation 3, 5, & 10 1/2 hours

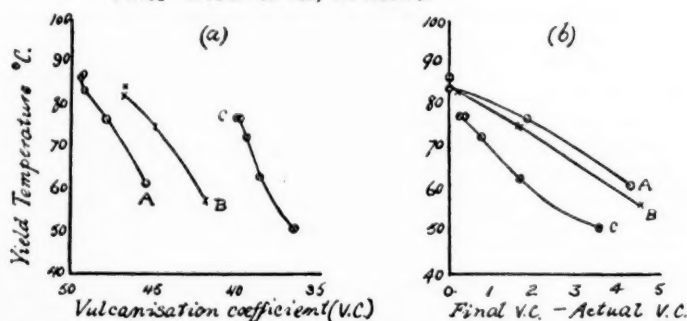


Fig. 20. Variation of yield temperature with (a) vulcanisation coefficient and (b) the difference between the final and actual V.C's. Mixings A, B, and C.

zation times almost coinciding. (3) The slope of the linear portion of the temperature-yield curve cannot be determined with great accuracy and shows no regular variation except that with mixing A it increases continuously. (4) The yield temperature increases rapidly while combination of sulfur is proceeding rapidly and becomes almost constant when combination ceases. (5) The general effect of these changes may be summed up by stating that, with each mixing, combination of sulfur with increasing time of vulcanization is accompanied by a movement of the whole temperature-yield curve in the direction of higher temperature, a limiting position being reached when combination ceases.

*Influence of Rubber-Sulfur Ratio.*—For equal periods of vulcanization the following effects of increasing the total sulfur content may be observed. (1) There is no substantial change in the general shape of the temperature-yield or time-yield curve. (2) The yield at any fixed temperature decreases continuously, but the difference between mixings A and B is very small for the three vulcanization times at which sulfur combination has practically ceased while there is still an excess of uncombined sulfur. The yields for the two longest vulcanization times with mixing C, where sulfur combination has practically ceased and there is no appreciable excess of uncombined sulfur, are practically equal but greater than for the corresponding vulcanization times of mixings A and B. (3) The slope of the linear portion of the temperature-yield curve decreases from C to B, but is practically the same on the average for A and B. (4) The yield temperature increases considerably from C to B and only slightly, though consistently for all vulcanization times from B to A. Mixing C is also different from A and B in that there is an appreciable increase in yield temperature between 5 and 7 hours, although there is practically none thereafter. This difference between C and the other mixings corresponds to differences in their properties with regard to continued combination of sulfur. (5) The general effect of these changes may be summed up by stating that, for each vulcanization time, increase of total sulfur content is accompanied by a movement of the temperature-yield curve in the direction of increasing temperature, the movement, however, being small when the vulcanization time is sufficient for sulfur combination to cease and the sulfur content is such as to leave an excess uncombined, even after prolonged vulcanization of 10.5 hours.

*Comparison with Previous Observations.*—Previous observations on plastic yield which are comparable with the present work are scanty. Kimura and Namikawa<sup>15</sup> obtained temperature-yield curves by a cantilever test and defined yield temperature in the same way as in this report, that is, by the intercept of the linear portion of the curve on the temperature axis. Yield temperature increased rapidly with increasing combined sulfur, but the separate factors of vulcanization time and rubber-sulfur ratio were inseparable, since all samples were given a prolonged vulcanization of 30 hours at 153° C. Paterson, Rayner, and Kinnes<sup>16</sup> used a similar definition of yield temperature, and obtained a value of 72° C for a 65/35 mixing of Para rubber and sulfur of unknown vulcanization time. The duration of stress was 2 hours.

### (3) Yield Temperature as an Index to Degree of Vulcanization

In the discussion on the chemical analyses of these materials it was pointed out that "vulcanization coefficient" by itself was unsatisfactory as an indication of degree of vulcanization except in relation to a single mixing. Plastic properties are so sensitive to vulcanization and so clearly dependent on the physical structure which gives hard rubber its distinctive properties as to justify

considering whether degree of vulcanization could be defined by plastic yield or yield temperature. Superficially, at least, this appears promising. The general similarity of the time-yield and temperature-yield curves for the fifteen materials under consideration indicates that, in spite of the complicated shapes of the curves, the properties may be defined approximately by, say, the yield temperature alone. It is clear also that, to some extent, an increase in temperature of test and a reduction in vulcanization time or sulfur content have equivalent effects.

This line of investigation has been followed independently by Kimura and Namikawa<sup>16</sup>, who, working with various rubber-sulfur ratios and prolonged vulcanization, determined the relation between softening point and percentage of combined sulfur, and found that the softening point corresponded to a transition between hard and soft states of hard rubber, at which the coefficient of thermal expansion also changed abruptly.

In Figure 20 (a), yield temperature is plotted against vulcanization coefficient, and it is seen that the connection is not a simple one. The curves for A and B are of similar shape but displaced from one another by an amount corresponding to a difference of vulcanization coefficient of about 3. The curve for C, however, as well as being similarly displaced is of rather different shape. Also, in all mixings there is a small but definite increase in yield temperature with prolonged vulcanization without further combination of sulfur.

If yield temperature is plotted against (final vulcanization coefficient—actual vulcanization coefficient) as in Figure 20 (b), the curves for A and B nearly coincide, but the curve for C lies apart, suggesting that in correlating the physical structure of various rubber-sulfur mixings with combination of sulfur, (1) a distinction must be made between mixings which are capable of retaining excess sulfur uncombined after long vulcanization and those which are deficient in sulfur, and (2) the difference from the final vulcanization coefficient for the mixing is more significant than the actual vulcanization coefficient, i.e., the coefficient as defined here, which is not necessarily the true coefficient. Conclusion (1) is supported by another fact. If the temperature-yield curves for all the mixings and vulcanization times are superposed, the curves for A and B form a regular family with practically no crossing over; whereas the curves for C show a greater tendency for yield to increase with temperature both in the steep linear portion (as shown by the greater slope in Table 12), and at the higher temperatures where yield has become less dependent on temperature.

## 8. PERMITTIVITY AND POWER FACTOR AT RADIO FREQUENCY

### (a) Method of Test

All the samples were tested for permittivity and power factor at 1000 kc. per sec. at 20° C and 60° C, so as to obtain information as to these properties at both low and high operating temperatures. In certain cases further information was obtained by tests at 40° and 75° C the latter temperature being included (1) to stimulate the limiting conditions contemplated by the Radio Research Board and (2) to confirm the authors' views on the dipole theory of dielectric loss in rubber-sulfur compounds. At the time the tests were undertaken, the work of Curtis, McPherson, and Scott<sup>17</sup>, and Kitchin<sup>18</sup> had shown that if the power factor and permittivity at normal temperature of fully vulcanized rubber-sulfur compounds of varying sulfur content were plotted against sulfur content, each property showed a sharp maximum between 0 and 19 per cent sulfur, and fell again to a normal value at about the latter percentage.

This was held to be in accordance with the theory of Boggs that the rubber-sulfur molecule becomes increasingly dipolar as the sulfur percentage increases up to a certain point, but that compensation later occurs, making the higher-sulfur compound nonpolar again. It was pointed out elsewhere in 1929 by one of the writers (Daynes) that the results were equally consistent with the view that no such compensation occurred, the fall in power factor and permittivity being due to increasing rigidity of the material, which took place fairly abruptly at a definite percentage of combined sulfur, and that if tests were carried out above the softening temperature, high values of power factor might be observed up to the highest possible percentage of combined sulfur. This view has been confirmed by the present tests, so far as they go, and by the more complete work of Kitchin<sup>9</sup>.

As a check on any permanent change due to the heating, samples were tested again at 20° C after testing at 60° C, the tests at 40° C and 75° C being made subsequently when required, the full sequence being 20°, 60°, 20°, 40°, 75° C. To allow for the material becoming stable, tests were made approximately 3 months after vulcanization. The tests were carried out by the National Physical Laboratory, from whose report the following information as to the method of test and results is taken.

The samples, on being received at the Laboratory, were cut into circles 23 cm. in diameter and the two surfaces were ground to a plane on sheets of emery cloth attached to a flat surface. No more of the surface layers was removed than was sufficient to render the samples reasonably flat. This was necessary to render the thickness of the sample capable of geometric definition and determination for the purpose of calculating the permittivity of the material.

The measurements were undertaken on the radio-frequency Schering Bridge developed at the Laboratory, using a frequency of one million cycles per second and mercury electrodes incorporating a guard ring device. The accuracy of the measurements was easily to 0.0001 in power factor. Any apparent inconsistencies in the results between different times of vulcanization would therefore appear to arise from lack of reproducibility in properties from separate mixings.

TABLE 13  
PRIMITIVITY AT 10<sup>6</sup> CYCLES PER SECOND

Mixing and nominal rubber-sulfur ratio	Vulcanization (hours at 155° C)	Permittivity at temperature				
		20° C	60° C	20° C	40° C	75° C
A 63/35	3	2.80	2.87	2.80	—	—
	3.75	2.82	2.86	2.82	—	—
	5	2.86	2.91	2.86	—	—
	7	2.88	2.90	2.88	—	—
	10.5	—	—	—	—	—
B 68/32	3	2.83	2.87	2.83	2.84	2.89
	3.75	2.81	2.86	2.81	2.83	2.87
	5	2.83	2.88	2.83	2.85	2.90
	7	2.83	2.88	2.83	2.85	—
	10.5	2.83	2.87	2.83	—	—
C 72/28	3	2.85	2.90	2.85	—	—
	3.75	2.80	2.85	2.80	—	—
	5	2.80	2.85	2.80	—	—
	7	2.80	2.85	2.80	—	—
	10.5	—	—	—	—	—

# (b) Results

The values obtained for permittivity and power factor are set out in Tables 13 and 14, respectively, and some of the results are plotted in Figures 21 and 22.

# (c) Discussion of Results

## Influence of Vulcanization Time

(i) *Permittivity*.—Changes of permittivity with vulcanization time are small and vary in direction according to the mixing. The greatest change is 3 per cent (A, 20° C, 3 to 7 hours). As vulcanization time is increased the permittivity of A increases, that of C decreases (between 3 and 3.75 hours), while that of B is practically unaffected. These conclusions apply both to 20° and 60° C.

TABLE 14

Mixing and nominal rubber-sulfur ratio		POWER FACTOR $\times 10^4$ AT $10^6$ CYCLES PER SECOND					Yield temperature (° C)	
		Vulcanization (hours at 155° C)	Power factor $\times 10^4$ at temperature					
			20° C	60° C	20° C	40° C		75° C
A 65/35	3	77	103	78	—	—	60.6	
	3.75	79	104	80	—	—	76.0	
	5	84	104	86	—	—	83.2	
	7	83	100	83	—	—	85.5	
	10.5	—	—	—	—	—	86.0	
B 68/32	3	78	111	78	87	163	56.5	
	3.75	86	106	86	96	118	74.5	
	5	88	110	89	100	117	82	
	7	87	107	88	98	—	83.5	
	10.5	90	111	91	—	—	83.5	
C 72/28	3	78	140	84	—	—	50.5	
	3.75	91	115	92	—	—	62.5	
	5	95	114	96	—	—	72.7	
	7	94	115	96	—	—	76.5	
	10.5	—	—	—	—	—	76.7	

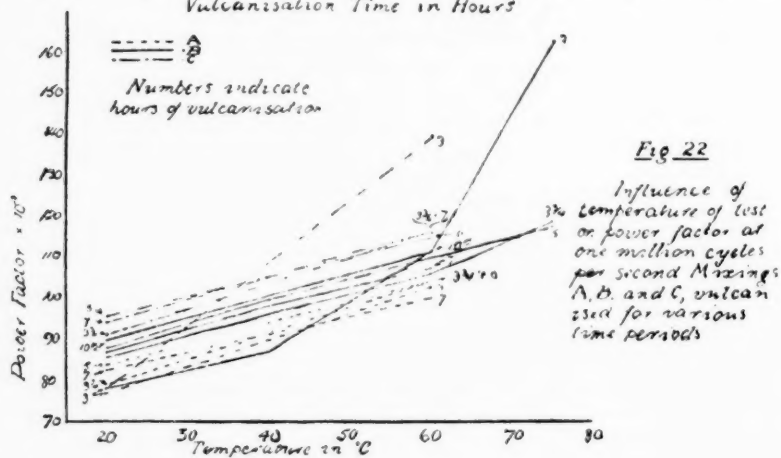
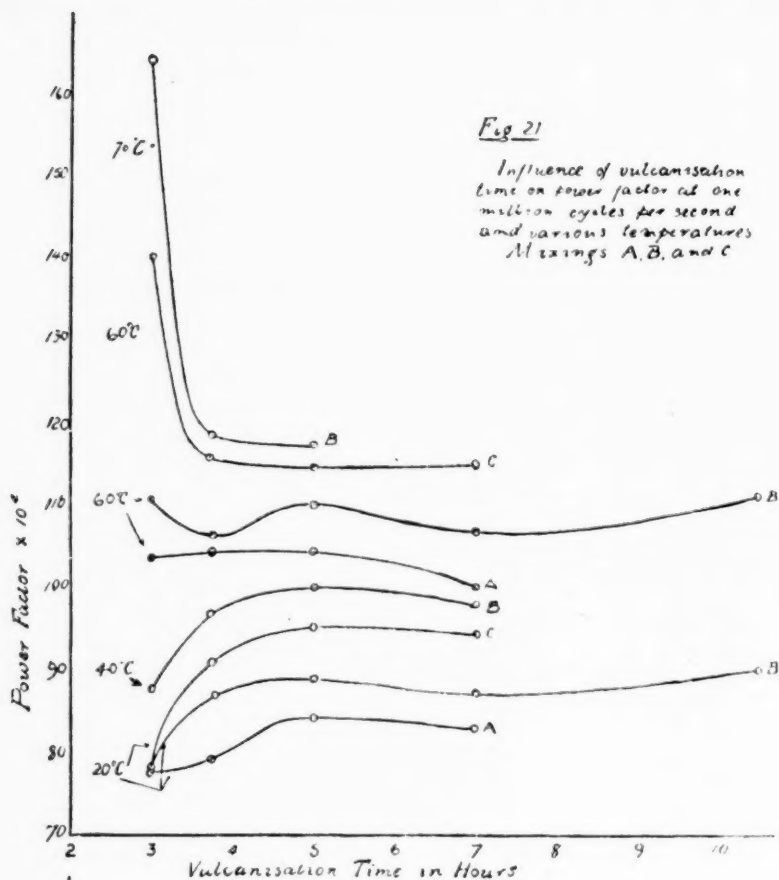
(ii) *Power Factor*.—At 20° C the power factor of each mixing increases up to about 5 hours, after which there is practically no change. The same applies to B at 40° C, A and C not being tested at this temperature. At 60° C A and B are practically unaffected by vulcanization time, whereas the power factor of C decreases considerably from 3 to 3.75 hours, after which there is no further change. At 75° C, B, the only mixing tested, decreases greatly in power factor from 3 to 3.75 hours, but no further between 3.75 and 5 hours.

## Influence of Rubber-Sulfur Ratio

(i) *Permittivity*.—The influence of rubber-sulfur ratio on permittivity is small, the greatest difference at any one temperature being 3 per cent (A and C, 20° C, 7 hours). For vulcanization times greater than 3.75 hours, mixing A had a higher permittivity than B, and B than C. For 3 hours' vulcanization the mixings are in the reverse order. These conclusions apply to temperatures of 20° and 60° C.

(ii) *Power Factor*.—For a given vulcanization time and temperature of test, C, has a higher power factor than B, and B than A. C has a particularly high power factor, relative to A and B, at 60° C when vulcanized for only 3 hours. There is a little doubt as to the true value for C, 3 hours, owing to the values at 20° C before and after heating to 60° C being appreciably different.





### Influence of Temperature of Test

(1) *Permittivity*.—Increase of temperature produces a small but regular increase of permittivity, the temperature coefficient not being influenced in any definite way or to any great extent by vulcanization time or rubber-sulfur ratio. The mean temperature coefficient is about 0.0012 per ° C.

(2) *Power Factor*.—In the majority of cases, power factor increases regularly with rise in temperature at the rate of about  $0.4 \times 10^{-4}$  per ° C, irrespective of mixing and vulcanization time. The notable exceptions are the samples with the shortest vulcanization time of 3 hours. The exceptional rise in these cases is most marked with C, mixings B and A following in descending order. At 75° C, only certain samples of mixing B were tested, but here again the abnormal increase for 3 hours' vulcanization is still more marked, and the 3.75-hour sample perceptibly increases in power factor relatively to the 5-hour sample, so that their order of merit is reversed. As was anticipated, the marked increase of power factor with temperature in certain cases appears to be closely associated with the mechanical softening at high temperatures, the abnormal increase, or departure from linearity of the temperature-power factor curve, occurring at about the yield temperature, and being greater the lower the yield temperature. For comparison, yield temperature is shown in the last column of Table 14.

### Comparison with Previous Observations

The only comparable work is that of Kitchin<sup>19</sup>, who tested a wide range of rubber-sulfur compounds at various temperatures and frequencies, including 1000 kc. per sec. The only sample comparable with the present samples was the limiting one containing 28.4 per cent combined sulfur and 3.3 per cent free

TABLE 15  
PERMITTIVITY AT 1000 KC. PER SEC. (KITCHIN)

Combined sulfur (%)	Permittivity at temperature			
	30° C	50° C	75° C	100° C
28.41	3.02	3.08	3.14	3.24
22.57	2.74	2.82	3.04	3.32

TABLE 16  
POWER FACTOR  $\times 10^4$  AT 1000 KC. PER SEC. (KITCHIN)

Combined sulfur (%)	Power factor $\times 10^4$ at temperature			
	30° C	50° C	75° C	100° C
28.41	68.8	82.5	197	471
22.57	81.0	184	511	890

sulfur, but the next, containing 22.6 per cent combined and 0.6 per cent free sulfur may be quoted to show the direction of the changes of properties with combined sulfur. The first sample may be compared roughly with B, 3 hours, but the second is much undervulcanized compared with C, 3 hours. Kitchin's results are shown in Tables 15 and 16.

For the full details of the complicated relations between electrical properties and frequency, temperature and composition, as well as the agreement of the results with those anticipated from the dipole theory of dielectric loss in rubber-sulfur compounds, reference must be made to the original paper. It may be recalled, however, that if power factor is plotted against the logarithm of

frequency for each of a series of temperatures and combined sulfur contents, the curves show maxima of about 9.1 per cent power factor, falling away on either side to low values of 1 per cent or less. The maximum is moved in the direction of higher frequency by an increase in temperature or a decrease in combined sulfur. If power factor is plotted against percentage of combined sulfur, there is a maximum which is moved in the direction of higher combined sulfur by a rise in temperature or a decrease in frequency.

As a result of these complicated relations, the influence of variables such as combined sulfur and temperature may be different in direction as well as magnitude at, say,  $10^3$  cycles per second from that at  $10^6$  cycles per second, so that it is not permissible to compare the present results with those of workers employing the lower frequency.

In the results of Kitchen it is not possible to separate the effects of rubber-sulfur ratio and degree of vulcanization, but the increases in permittivity and power factor with rising temperature are shown, the temperature coefficient of permittivity being greater ( $0.0027$  per  $^{\circ}\text{C}$ ) than found in the present investigation.

## 9. ELECTRIC STRENGTH

### (a) Method of Test

The sheets tested were five in number, selected to show the influence of vulcanization time and rubber-sulfur ratio, but they were not quite comparable with the remainder of the sheets used in this investigation in that (1) they were not vulcanized simultaneously with the other sheets; (2) they were of double thickness ( $\frac{3}{8}$ -inch), (3) they were vulcanized for slightly shorter times so that the effective vulcanization times were 3, 5, and 10.5 hours, including the effect of vulcanization during the rise, and (4) the rubber had not been averaged.

The breakdown was effected between 1-inch diameter steel balls on a minimum thickness of 1 mm.; the depression was machined in the manner described in British Standard Specification No. 234-1931. All tests were made under oil at room temperature ( $19.8^{\circ}\text{C}$ ), the voltage being raised slowly until breakdown took place. Four tests were made on each grade; the R.M.S. voltage across the specimen was read on an electrostatic voltmeter used with capacitative potential divider and freshly calibrated with standard 62.5 mm. spheres. It is estimated that the maximum possible error in calibration reading and measuring the thickness would be about 8 per cent.

### (b) Results

The results are shown in Table 17.

TABLE 17  
ELECTRIC STRENGTH

Mixing and nominal rubber-sulfur ratio	Vulcanization (hours at $155^{\circ}\text{C}$ )	Electric strength (volts (R.M.S.) per mm.)			Range of variation (% on mean)
		Maximum	Mean	Minimum	
P, 65/35	$4\frac{3}{4}$	105800	88450* (97600)	61000* (84500)	(+8, -13)
Q, 68/32	$2\frac{3}{4}$	105800	93500	86500	+13, -8
Q, 68/32	$4\frac{3}{4}$	93500	88625	82500	+6, -7
Q, 68/32	10	102500	95200	88500	+8, -7
R, 72/28	$4\frac{3}{4}$	123000	109350	90600	+13, -21

\* Neglecting low value of 61000 volts per mm. which, as puncture was off center, was probably due to fault in the material, the minimum, mean, and range of variation were as shown in brackets.

(c) *Discussion of Results*

Owing to the well known variability of electric strength determinations there must be some uncertainty as to the extent to which small variations in breakdown strength should be considered as real effects. In some of the tests recorded above the variation is large; in fact the ranges of variation of the results on all five sheets overlap over the range 90600 to 93500 volts per mm.

The mean results indicate the following relations.

*Influence of Vulcanization Time.*—In the only case, mixing Q, in which vulcanization time was varied, there is a minimum electric strength, the value for 4½ hours being less than either 2½ or 10 hours.

*Influence of Rubber-Sulfur Ratio.*—For the only vulcanization time, 4½ hours, where the rubber-sulfur ratio was varied, there was a minimum electric strength, the value for mixing Q being appreciably less than that for mixing P and much less than for mixing R.

*Comparison with Previous Literature.*—There are numerous published determinations of electric strength of high-grade hard rubber giving values up to 150 kV per mm., but in no case are both the composition and vulcanization stated. Curtis, McPherson, and Scott<sup>17</sup> made some observation on rubber-sulfur compounds of different sulfur contents, the uncombined sulfur being negligible in amount. Without quoting figures, they stated that, while there did appear to be some relation between composition and dielectric strength, factors other than composition gave rise to variation of much larger magnitude.

10. VOLUME AND SURFACE RESISTIVITY; DISCOLORATION AND CHANGES OF SURFACE RESISTIVITY ON EXPOSURE TO LIGHT

(a) *Methods of Test*

(i) *Decrease in Surface Resistivity on Exposure to Light*

On exposure to light, hard rubber rapidly forms a conducting film of sulfuric acid which, if not removed spoils the material as an insulator. The method adopted for investigating the changes in insulating value is briefly as follows. A thin strip of each material is provided with Aquadag electrodes and suspended in a Vita-glass tube, one face of the sample being directed towards north daylight, and measurements of the resistance are made from time to time by observing the rate of charge of the needle of a Lindemann electrometer when the specimen is connected between the needle and a source of high potential. The samples being compared are exposed simultaneously so that the light conditions are similar for all, but the exposure is measured approximately in terms of the darkening of a photographic paper. During exposure and measurement, the humidity of the atmosphere in the tubes is maintained at 75 per cent relative humidity by the presence of moist sodium chloride.

The following are the standard conditions of test adopted in the present work: length of test-piece, 50 mm.; width of test-piece, 10 mm.; thickness of test-piece, 1 mm.

The long edges of the test piece were coated with Aquadag, having a central, uncoated strip 5 mm. wide on both faces, so that the length and width of the leakage path on the exposed face were 5 mm. and 50 mm. respectively.

Resistivity was measured 2 minutes after application of a potential of about 200 volts. Humidity of atmosphere during exposure and measurement, 75 per cent relative humidity.

A "standard hour" of daylight is defined as an hour of light of such intensity that it darkens a Watkins Bee meter to the standard shade in 20 seconds. An

hour of light which produces the same effect in  $x$  seconds is called  $20/x$  "standard hours". This definition is, of course, unsuitable for determining the intensity in absolute units, but as all the samples concerned were exposed simultaneously and the same photographic paper was used throughout the exposures, the estimation of the relative merits of the samples is not affected by any uncertainty as to the absolute intensity.

### (ii) Discoloration on Exposure to Light

To find whether the greenish discoloration which takes place on exposure to sunlight runs parallel to the changes in surface resistivity, samples of mixings A, B, and C, vulcanized for 3 and 10.5 hours, were exposed simultaneously for many months in daylight under ordinary atmospheric conditions. After the colors had been compared, the discoloration was intensified by dipping the exposed samples momentarily into boiling water, and the surfaces were compared again visually.

### (iii) Volume Resistivity

Owing to the high value of the volume resistivity of hard rubber of the quality under test, it was considered that accurate determination of the relative merits of the various samples in this respect was unnecessary. It will be realized, however, that before the freshly cleaned sample is exposed to light, the leakage is through the body of the material, so the apparent surface resistivity at that stage is a measure of the volume resistivity if the dimensions of the sample are standardized, as in the present case. With these test-pieces, the volume resistivity in ohm-cm. can be obtained approximately by multiplying the initial apparent surface resistivity by 0.05.

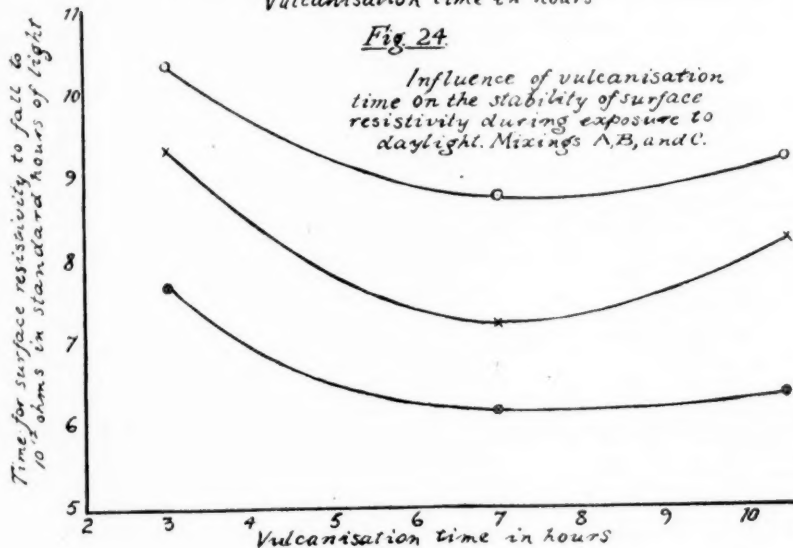
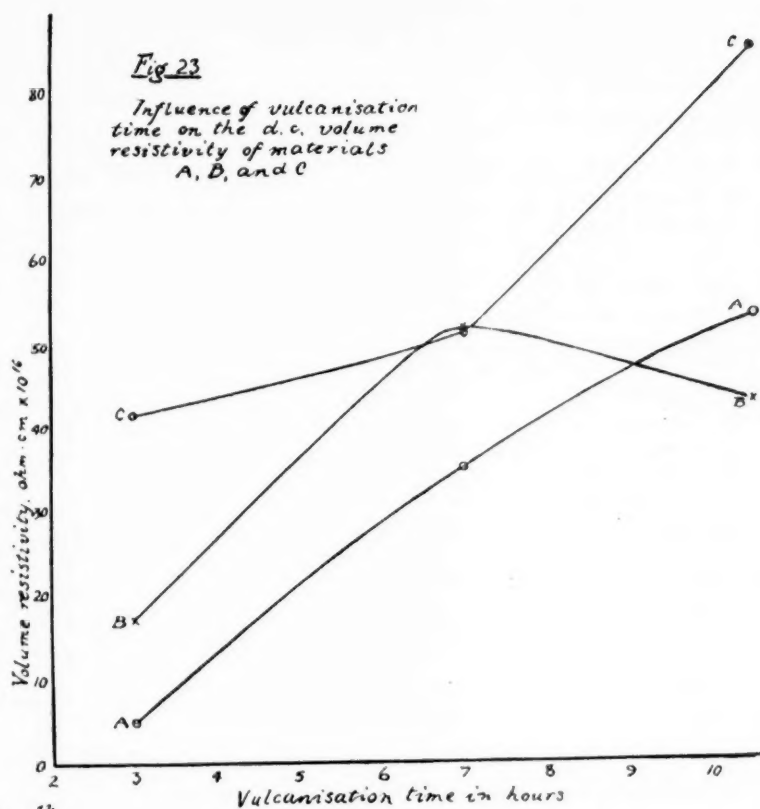
TABLE 18  
SURFACE DETERIORATION AS SHOWN BY CHANGES IN SURFACE RESISTIVITY

Mixing and nominal rubber-sulfur ratio	Vulcanization (hours at 155° C)	Apparent initial surface resistivity (ohms $\times 10^{12}$ )	Time of exposure in "standard hours" of sunlight to fall to surface resistivity, in ohms			
			$10^{18}$	$10^{15}$	$10^{12}$	$10^9$
A 65/35	3	8.94	—	7.1	10.3	19
	7	68.6	4.4	6.2	8.7	15
	10.5	106	4.7	6.6	9.1	16
B 68/32	3	32.6	4.0	6.0	9.3	17.5
	7	104	3.5	5.0	7.1	12.5
	10.5	85.8	3.7	5.5	8.1	14
C 72/28	3	82.4	3.1	4.9	7.6	15.5
	7	103	2.3	3.8	6.1	11
	10.5	171	2.5	4.0	6.2	10.5

### (b) Results

#### (i) Decrease in Surface Resistivity on Exposure to Light

In Table 18 will be found the times taken for the various materials tested to fall to  $10^{18}$ ,  $10^{15}$ ,  $10^{12}$ , and  $10^9$  ohms in apparent surface resistivity, as well as the initial values on sandpapered, unexposed material. There is a short period during which the volume leakage is dominant, so there is no apparent change in surface resistivity. This period varied from about 2 to 4 standard hours in mixings C to A, respectively.





## (ii) Discoloration on Exposure to Light

The discoloration was greatest with mixing C and least with mixing A. In each case the sample vulcanized for 10.5 hours was more discolored than the 3-hour sample, but the difference was slight compared with the quite distinct difference between the three mixings.

## (iii) Initial Volume Resistivity

As already explained this quantity is approximately one-twentieth of the value shown in column 3 of Table 18.

## (c) Discussion of Results

## Influence of Vulcanization Time

(i) As shown by surface resistivity tests, each mixing appears to be less stable with a medium vulcanization time than with a short or long vulcanization, though the change in stability is most marked between 3 and 7 hours.

(ii) Discoloration observations agree with electrical results in that the 3-hour sample is in each case less changed by exposure than the 10.5-hour sample, but the difference is not very marked.

(iii) The general tendency is for volume resistivity to increase considerably with increasing vulcanization time, but the results are not quite regular.

## Influence of Rubber-Sulfur Ratio

(i) The higher the sulfur content the slower is the fall in surface resistivity on exposure to light, A, B, and C being in descending order of merit in this respect.

(ii) Discoloration observations agree with electrical results in that A, B, and C are in descending order of merit.

(iii) In respect of volume resistivity, C, B, and A are generally in descending order of merit, but the results are not quite regular. This is in agreement with the observations of Curtis, McPherson, and Scott<sup>17</sup>, who found values  $2.9 \times 10^{16}$  and  $3.12 \times 10^{16}$  ohm-cm. for fully vulcanized compounds having rubber-sulfur ratios 68/32 and 71.5/28.5, respectively. These absolute values are lower, no doubt partly due to electrification for only 1 minute, but the direction of the difference is the same as found in the present work.

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- <sup>3</sup> Glancy, Wright and Oon, *Ind. Eng. Chem.* 18, 73 (1926).
- <sup>4</sup> Marchandise, "Encyclopédie du Caoutchouc et des Industries qui s'y Rattachent", Paris, 1929, p. 333.
- <sup>5</sup> Ramondt, "Het een en ander over Eboniet", Lecture, Nov. 11, 1904.
- <sup>6</sup> See also *J. Rubber Research* 7, 123 (1938).
- <sup>7</sup> Dieterich and Gray, *Ind. Eng. Chem.* 18, 428 (1926); Schering, "Die Isolierstoffe der Elektrotechnik", Berlin, 1924.
- <sup>8</sup> See also *Trans. Inst. Rubber Ind.* 13, 96 (1937).
- <sup>9</sup> Ariano, *L'Industria* 43, Nos. 17, 18, 19 (1929).
- <sup>10</sup> Flight, *Institution of the Rubber Industry Year Book* 2, 386 (1923); *India-Rubber J.* 65, 967, 1007 (1923).
- <sup>11</sup> Dieterich and Gray, *Ind. Eng. Chem.* 18, 428 (1926).
- <sup>12</sup> Geisler, "Künstlicher Kautschuk für elektrische Isolierungszwecke", Berlin, 1922, p. 56-66.
- <sup>13</sup> Schering, "Die Isolierstoffe der Elektrotechnik", Berlin, 1924.
- <sup>14</sup> See also *J. Research Assoc. Brit. Rubber Manufacturers* 5, 11 (1936); *J. Rubber Research* 8, 41 (1939).
- <sup>15</sup> Kimura and Namikawa, *J. Soc. Chem. Ind. Japan* 32, 196b (1929); main binding (Japanese text), p. 653 for graphs.
- <sup>16</sup> Paterson, Rayner and Kinnes, *J. Inst. Elec. Eng.* 50, 217 (1913); *India-Rubber J.* 45, 823 (1913).
- <sup>17</sup> Curtis, McPherson and Scott, *Bur. Standards, Sci. Paper No. 560*, 1927, pp. 398-418.
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- <sup>19</sup> Kitchin, *Ind. Eng. Chem.* 24, 549 (1932).

PROPERTIES OF HARD RUBBER. XVII. INFLUENCE  
OF RUBBER-SULFUR RATIO AND VULCANIZA-  
TION TIME ON THE PROPERTIES OF PURE  
RUBBER-SULFUR COMPOSITIONS. (3)  
SWELLING, WATER ABSORPTION,  
AGING, AND A GENERAL  
DISCUSSION OF RESULTS \*

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I (a). B. METHODS OF TEST AND RESULTS

11. SWELLING IN ORGANIC LIQUIDS

(a) *Method of Test.*—The materials selected were A, 5 hours, and C, 3.75 hours. It was not possible to include sufficient samples to show the separate effects of varying vulcanization time and rubber-sulfur ratio, but the samples show the effect of a considerable difference in combined sulfur, having vulcanization coefficients of 49.5 and 38.7, respectively.

To show the dependence of swelling on the nature of the liquid, tests were carried out in twenty different liquids selected to represent various chemical types. Each piece of hard rubber, measuring  $20 \times 19 \times 5.5$  mm., was placed in a stoppered bottle with about 40 cc. of the liquid under examination. The bottle was kept in a thermostat at  $34^{\circ}\text{C}$  and shielded from light. The test-piece was then weighed after various periods of immersion ranging from 4 to 4000 hours. The absorption of liquid after each period was calculated from the increase in weight and expressed by the volume of liquid absorbed as a percentage of the initial volume of the test-piece.

(b) *Results.*—No sign of solution of the rubber-sulfur compound was observed, but in certain cases, where swelling was rapid, cracking occurred. In three cases this took place before the first weighing could be made. Full-time swelling curves were obtained, but as most of the liquids are not likely to come into regular contact with hard rubber in electrical service, figures are given in Table 19 for one long and one short period only. In this table, swelling less than 1 per cent is shown as zero. Closer readings for certain liquids of very low absorption are shown in Table 20.

Swelling after 4000 hours was about 0.2 per cent or less with the following:—Petroleum ether (A), paraffin (A), transformer oil (A and C), decalin (A), alcohol (A and C), glycerol (A and C), linseed oil (A and C), castor oil (A and C). Other cases of interest where swelling after 4000 hours was between 0.2 and 1 per cent are shown in Table 20.

(c) *Discussion of Results.*—The principal results of interest in connection with the present work are as follows:—

(i) With some liquids the swelling is considerable and may be associated with cracking; with others it is negligible. The actual swelling is tabulated

\* Reprinted from the *Journal of Rubber Research*, Vol. 15, No. 8, pages 163-179, August 1946.

TABLE 19  
SWELLING (PERCENTAGE BY VOLUME) IN VARIOUS LIQUIDS

Class of liquid	Liquid	Sample	Swelling (% by volume) at 34° C during		Interval during which cracking occurred (hrs.)
			24 hrs.	4000 hrs.	
Saturated hydrocarbons	Petroleum ether, free from aromatic hydrocarbons (b.p. 60–80° C)	A	0	0	—
		C	0	approx. 10*	—
	Paraffin, lamp oil (b.p. 180–280° C)	A and C	0	0	—
	Transformer oil	A and C	0	0	—
Hydroaromatic hydrocarbons	Cyclohexane	A	0	0	—
		C	3	49	—
	Decalin (commercial decahydronaphthalene) (b.p. 187–193° C)	A	0	0	—
		C	1	7	—
Aromatic hydrocarbons	Benzene	A	12	—	150–199
		C	36	—	7–24
	Xylene (commercial “purified”)	A	5	70	—
		C	23	—	33–50
Organic halogen derivatives	Carbon tetrachloride	A	1	—	1440–2190
		C	15	—	80–97
	Chlorobenzene	A	20	—	50–74
		C	56	—	5–9
Organic sulfur derivative	Carbon disulfide	A	79	—	0–4
		C	107	—	0–4
	Ethyl alcohol (absolute)	A and C	0	0	—
	Acetone	A	0	4	—
Organic compounds containing polar groups		C	2	16	—
	Ethyl acetate	A	0	7	—
		C	3	26	—
	Glycerol	A and C	0	0	—
	Nitrobenzene	A	2	61	—
		C	7	95	—
	<i>o</i> -cresol	A	1	47	—
		C	5	—	1057–1274
	Aniline	A	0	17	—
		C	3	64	—
	Linseed oil	A and C	0	0	—
	Castor oil	A and C	0	0	—
Water		A and C	0	0	—

\* Eight at 2200 hours

above, and the results with individual liquids call for no further comment in a report dealing primarily with hard rubber for electrical purposes. The following generalization as to the influence of the swelling liquid, however, may be noted. The influence of the liquid varies according to the degree of vulcanization, the swelling being reduced in different proportions by complete vulcanization. In general, swelling is small with the saturated hydrocarbons, hydroaromatic hydrocarbons, and fat oils; high with aromatic hydrocarbons, halogenated hydrocarbons, and carbon disulfide, and intermediate or small with polar compounds. The low swelling with the saturated hydrocarbons, *e.g.*, transformer oil, is of particular interest in connection with electrical equipment and is remarkable in view of their strong swelling action on soft rubber.

TABLE 20  
SWELLING IN CERTAIN LIQUIDS

Liquid	Sample	Swelling (% by volume) after:		
		350 hours	2000 hours	4000 hours
Paraffin	C	0.2	0.4	0.5
Cyclohexane	A	—	0.1	0.4
Water	C	0.1	0.2	0.3

(ii) The comparison of a fully vulcanized high-sulfur compound and an undervulcanized low-sulfur compound cannot show the separate effects of vulcanization time and rubber-sulfur ratio. It may be stated, however, that with each liquid the swelling action decreases with increase in the vulcanization coefficient but that the rate of decrease depends on the nature of the liquid. Thus in every case C, 3.75 hours, was swollen more than A, 5 hours, and cracked, if at all, in a shorter time. The original curves also showed that C, 3.75 hours, approached saturation more quickly than A, 5 hours, apparently because it was more permeable to the liquid. This difference between the swelling of A and C is most pronounced with liquids having only a weak swelling action, such as petroleum ether, decalin, cyclohexane, acetone, and ethyl acetate, and is in fact strikingly large, considering the comparatively small difference in the vulcanization coefficients. On the other hand, swelling, though reduced by increased vulcanization, is not negligible even with the fully vulcanized sample A, 5 hours, in aromatic hydrocarbons, halogenated hydrocarbons, and carbon disulfide.

(iii) No conclusion may be drawn as to the swelling at high temperatures. All tests were made at 34° C, but in view of the marked change in the physical structure of hard rubber at temperatures about 50–80° C, the same relations cannot be assumed to hold at the higher temperatures. However, any changes in swelling due to reversible changes in physical structure may be expected to occur at higher temperatures with A than with C, which has a much lower yield temperature. Dunton and Muir<sup>1</sup> state that hard rubber is "badly cracked" by 7 days' immersion in hot transformer oil.

## 12. ABSORPTION OF WATER AT EQUILIBRIUM

(a) *Method of Test.*—Three samples of each mixing, vulcanized for 3, 5, and 10.5 hours, respectively, were selected for water absorption tests. Finely rasped samples of about 1.5 grams of each material were stored for 24 hours on tared carriers over calcium chloride in closed vessels, and, after weighing, were

transferred to similar vessels containing damp potassium sulfate (relative humidity 97.2 per cent) and stored at 20° C. They were then weighed at intervals up to 6 days after the change of humidity, after which they were stored dry again and weighed at intervals up to 7 days. Weighing was carried out without removing the samples from the controlled atmosphere. Throughout the tests a blank determination was carried out with an empty carrier to correct for absorption by the watchglass. The corrected results are calculated on the initial dry weight of the material immediately before the increase of humidity to 97.2 per cent relative humidity.

(b) *Results.*—The absorption of water, expressed as percentage by volume (the density of each sample being known) is shown in Table 21.

TABLE 21  
WATER ABSORPTION AT EQUILIBRIUM

Mixing and nominal rubber-sulfur ratio	Vulcanization (hrs. at 155° C)	Water absorption by volume, %, after:									
		Period at 97 per cent relative humidity (days)					Subsequent period at 0 per cent relative humidity (days)				
		6-7 24	3	4	5	6	1 48	1	2	4	7
A 65/35	3	0.38	0.46	0.50	0.49	0.51	0.09	0.05	0.04	0.05	0.06
	5	0.42	0.47	0.51	0.49	0.51	0.12	0.10	0.08	0.10	0.11
	10.5	0.38	0.43	0.44	0.44	0.44	0.08	0.06	0.04	0.07	0.07
B 68/32	3	0.38	0.45	0.48	0.48	0.49	0.10	0.05	0.02	0.05	0.04
	5	0.39	0.44	0.45	0.45	0.45	0.08	0.05	0.04	0.06	0.06
	10.5	0.39	0.45	0.45	0.45	0.45	0.08	0.07	0.06	0.06	0.07
C 72/28	3	0.41	0.50	0.53	0.53	0.54	0.12	0.06	0.04	0.06	0.08
	5	0.38	0.44	0.45	0.46	0.46	0.09	0.05	0.05	0.05	0.08
	10.5	0.42	0.47	0.47	0.48	0.48	0.08	0.06	0.05	0.05	0.09

It is seen that in most cases the weight has become practically steady after 3 days at 97.2 per cent relative humidity, as would be expected from previous experience. In some cases, however, principally the 3-hour samples, the weight increases throughout the 6 days. Moreover, on drying, the original dry weight is not recovered; in fact, after a minimum at about 2 days under dry conditions the weight increases again. It is possible that this increase under both dry and moist conditions is due to rapid oxidation of the material in its finely divided state. The increase of weight of sample A, 5 hours, when redried, above its original dry weight is consistently higher than all the other samples, suggesting that there may have been an error in the initial dry weight, in which case 0.03 per cent should be deducted from the absorption figures for that sample in Table 21 for comparative purposes.

### (c) Discussion of Results

*Influence of Vulcanization Time.*—After about 6 to 7 hours at 97.2 per cent relative humidity, by which time most of the absorption has occurred, no definite influence of vulcanization time is perceptible. After 6 days the absorption by each of the 3-hour samples has increased appreciably above that of the other samples of the same mixing. Whether this is due to the water-absorbent properties of the material or to a secondary effect of oxidation is not clear. If the latter is the explanation it would appear that the undervulcanized

samples are more prone to oxidation or that their oxidation products are more absorbent.

*Influence of Rubber-Sulfur Ratio.*—There is an indication that mixing C has a higher absorption than A and B throughout the period of exposure, but the excess is slight and scarcely beyond the limits of error of measurement.

### 13. DETERIORATION IN AIR AT 70° C

It may be recalled that in the case of soft vulcanized rubber the search for a perfect accelerated aging test has lasted for many years and the need for such a test is to some extent still unsatisfied. In the case of hard rubber, so far as may be judged from published papers, the subject has received very little attention. It was not anticipated, therefore, that reliable information could be obtained in a short time on the relative merits of the present samples in respect to aging; but some preliminary tests were undertaken to select a technique which would give at least some tentative ideas on the subject.

These preliminary tests were carried out on a 70/30 rubber-sulfur mixing vulcanized for 5 hours at 155° C. The investigation has been described in a separate report<sup>2</sup>, the principal conclusions being that: (1) marked deterioration occurs after different periods, according to the property tested; thus, impact strength may be quickly reduced, while cross-breaking strength is not affected for many months; (2) with unnotched test-pieces, deterioration occurs less rapidly if the test-pieces are cut from the sheet after aging instead of being aged as test-pieces; (3) deterioration is confined to the surface; if the surface layers are removed before test the impact strength of both types of test-piece is found to be unimpaired even after long periods; (4) the plastic yield temperature increases considerably on aging at 70° C for 200 days.

(a) *Method of Test.*—For the purposes of the present investigation the following properties were adopted as a criterion of the relative degrees of resistance of the materials to the action of hot air: (1) impact strength of unnotched test-pieces, (2) impact strength of notched test-pieces, the test-pieces being prepared before aging in both cases. The aging period (10 weeks) was not sufficient for a reliable indication of the relative changes in plastic yield temperature of the various materials. For exposure in a ventilated thermostat at 70° C, special racks were so designed that the test-pieces were free from serious mechanical strain, but so that all faces were freely exposed to air. Impact tests were carried out according to Method 2, at least two days being allowed to elapse between removal from the oven and testing<sup>3</sup>.

(b) *Results.*—The results are shown in Tables 22 and 23.

TABLE 22  
IMPACT STRENGTH OF UNNOTCHED TEST PIECES

Mixing and nominal rubber-sulfur ratio	Vulcanization (hrs. at 155° C)	Impact strength (kg.-cm. per sq. cm.) after aging period in air at 70° C (weeks)			
		0	2	6	10
K 65/35	3	43	45	49	52
	5	42	29	28	25
	10.5	46	44	45	44
L 70/30	3	59	53	50	35
	5	48	32	28	24
	10.5	54	41	47.5	41



TABLE 23  
IMPACT STRENGTH OF NOTCHED TEST-PIECES

Mixing and nominal rubber- sulfur ratio	Vulcanization (hrs. at 155° C)	Impact strength (kg.-cm. per sq. cm.) after aging period in air at 70° C (weeks)			
		0	2	6	10
K 65/35	3	2.0	2.5	2.2	2.5
	15	1.9	2.1	2.3	2.4
	10.5	1.6	1.8	2.4	2.0
L 70/30	3	2.6	3.25	2.6	2.5
	5	2.1	2.35	2.5	2.5
	10.5	1.9	2.05	2.15	2.3

(c) *Discussion of Results.*—It has been pointed out<sup>3</sup> in Section 6 that, although the technique of impact testing appears capable of giving reasonably consistent results on a uniform material, there appear to be some variables in the manufacture of the test-sheets and(or) in the preparation of the test-pieces which produce real differences of impact strength in nominally identical materials, without appreciably affecting such properties as cross-breaking strength and plastic yield temperature. Examples of this will be found in a comparison of the results in this Section with those of Section 6 as well as with those of a previous report on the aging of hard rubber<sup>2</sup>. When it is considered also that the selection of the conditions to which the samples were exposed during their aging periods was based on very little experience of testing the aging properties of hard rubber, it will be appreciated that the present results must be applied with caution, and that confirmation of certain points at a later time, when more is known about the factors which affect the impact strength, is very desirable.

#### Influence of Vulcanization Time

(i) *Unnotched Test-Pieces.*—The impact strengths of the 3- and 10.5-hour samples are in reasonable agreement with those found with independently made samples in Section 6, but the strength of the 5-hour sample is low with each mixing. Consequently there is a minimum strength at 5 hours instead of a maximum as previously found by three different methods. No reason can be offered for this difference; microporosity was suspected, but tests of density showed no abnormality. It is clear that the 5-hour sample of each mixing deteriorates more rapidly than the corresponding 3- and 10.5-hour samples; but the latter do not differ much from one another in rate of deterioration. It is possible that the more rapid deterioration of the 5-hour sample is due to the same factor as is responsible for their low initial strength.

(ii) *Notched Test-Pieces.*—The initial strengths of these samples do not show such a rapid fall in strength from 3 to 5 hours as do those of Section 6; otherwise the general effect of vulcanization time is confirmed, the values for K, 5 and 10.5 hours, agreeing well with the corresponding values for A, which is nominally the same mixing. There appears to be no deterioration during 10 weeks in air at 70° C, most of the samples increasing considerably in strength in that period. The extent to which this improvement takes place does not appear on the whole to be appreciably affected by vulcanization time. This improvement with exposure is not in accordance with the results previously obtained with a 70/30 mixing vulcanized for 5 hours in a preliminary aging program, when a definite fall of strength was observed. No explanation of this difference can be offered, but it will be noted that the initial strengths were very

different in the two cases, those of the present samples being much lower, whereas the final values obtained after the period of aging were approximately the same.

### Influence of Rubber-Sulfur Ratio

(i) *Unnotched Test-Pieces*.—As one would expect from a mixing with a rubber-sulfur ratio between 68/32 and 72/28 (see Section 6), mixing L is consistently superior in initial impact strength to mixing K. In all cases, however, L deteriorates more rapidly, so that after 10 weeks' exposure it is inferior to K. This is most marked in the 3-hour samples, where the strength of L has fallen about 40 per cent, while that of K has increased.

(ii) *Notched Test-Piece*.—The initial strength of L is slightly higher than that of K, as might be expected from interpolation between the values of Table 7 (Section 6); but the degree of superiority of L over K is small compared with that of C over A. There appears, on the whole, to be no appreciable influence of rubber-sulfur ratio on the increase in strength during the 10 weeks of exposure to air at 70° C.

### Comparison With Previous Observations

The only comparable work published in detail appears to be that of Dieterich and Gray<sup>4</sup>, who studied the effect of exposure to air at high temperatures on a variety of hard rubbers, containing various accelerators and mineral ingredients. The only mixing strictly comparable with the present ones was one having a rubber-sulfur ratio 71.43/28.57 and vulcanized for 12 hours at 149° C. This was tested for cross-breaking strength and impact strength (unnotched) before and after 14 days in air at 70° C and, in addition, for plastic yield temperature and the same two properties after 25 and 60 hours in air at 149° C. During the air treatment at 70° C the impact strength fell from 41.2 to 25.8 kg.-cm. per sq. cm., while cross-breaking strength rose from 859 to 1050 kg. per sq. cm.; this is qualitatively in agreement with the findings of the present investigation. In the exposure at 149° C the influence of oxidation is complicated by the simultaneous prolonged overvulcanization of the interior of the samples. In this case, during exposures of 25 and 60 hours, impact strength changed from 41.2 to 6.4 and 2.3 kg.-cm. per sq. cm., and cross-breaking strength from 859 to 992 and 485 kg. per sq. cm. respectively, while yield temperature rose from 78° C to 83° C after 25 hours.

### A. RELATIVE MERITS OF MIXINGS AND VULCANIZATION TIMES

#### (i) Relative Importance of Various Properties

It is clear that there is no single mixing and vulcanization time which gives optimum results in all properties, so it is necessary to select either a single material which has good all-around performance or, say, two materials from which selection may be made according to the property which is most important for the application in view. This involves deciding on the relative importance of the various properties tested, a decision which can only be based on a consensus of opinion among designers and users of insulating materials. It may be recalled that the present investigation was undertaken primarily to improve hard rubber for radio-frequency uses, so the following discussion will be governed by that consideration. The following notes will indicate briefly the estimates of the importance of various properties for the purpose of the discussion.

*Free Sulfur.*—It is usually assumed that free sulfur is responsible for corrosion of adjacent metal parts, although the authors are not aware of any scientific study of the subject. It is certain that in some cases the formation of sulfuric acid has been wrongly attributed to the free sulfur, for example, in the case of hard rubber exposed to sunlight, but it will be accepted that, other things being equal, a high percentage of free sulfur is probably undesirable.

*Density and Coefficient of Thermal Expansion.*—Small changes of density are of little importance. Coefficient of expansion should preferably be reduced to a value comparable with that of the common constructional metals; but this is becoming of less importance in view of the practice of supporting insulated components on metal frames instead of on large panels of insulating material.

*Tensile Properties.*—Tensile strength and elongation were measured as more fundamental properties than cross-breaking strength and deflection, although the latter correspond more closely to the requirements in the majority of uses. Rigidity as indicated by Young's modulus is treated as a useful but not one of the most important properties. Resilient energy was included with the object of obtaining some correlation with impact strength; its value as a property in service is doubtful, but it may perhaps be taken as an indication of the ability of the material to absorb tensile shocks in certain uses.

*Cross-breaking Strength and Deflection.*—Cross-breaking strength seems to be accepted as a useful test of strength, being frequently referred to in specifications. In the present tests, cross-breaking strength and tensile strength appear to vary in practically constant ratio, which renders their consideration as separate properties unnecessary. The value of cross-breaking "elongation" is less certain. For a given cross-breaking strength a high "elongation" no doubt indicates a tendency not to be easily broken where either the range of movement or the kinetic energy of an object deflecting or striking it is limited. As, however, much of the deflection at high loads near the breaking point is of the nature of permanent deflection, it is difficult to decide to what extent the high deflection should be counted as an advantage.

*Impact strength.*—There appears to be no justification for adopting either the notched or unnotched test-piece alone in impact testing, since different properties appear to be involved. It is obvious, however, that the notch has a serious weakening effect and so should be avoided where possible in designing. When unnotched, hard rubber is outstanding in its ability to absorb energy in deformation without breaking. In view of its superiority in this respect it will be assumed that variations in strength when unnotched are less important than variations of strength when notched.

*Plastic Yield and Yield Temperature.*—These are, of course, recognized as of fundamental importance, as indicated by the practice of classifying materials on this basis. It was in these respects that improvement in hard rubber was most desired as a result of this program of research.

*Permittivity and Power Factor.*—The product of these, called the loss factor, is of fundamental importance for radio reception and transmission, though there may be many applications in which they are of no interest. Loss factor when the material is cold is of importance in receiving apparatus. Loss factor when the material is hot is of importance in receiving apparatus used under tropical conditions, but it is chiefly of importance in transmission, where the material may be heated by high-frequency, high-stress oscillations. In these cases a high loss factor when hot is a serious disadvantage both in accelerating electrical breakdown and also in producing mechanical failure through soften-

ing. Loss factor at room temperature will, therefore, be treated as less important than at elevated temperatures.

*Electric Strength.*—In some quarters there is a tendency for an electric strength test to be regarded as a useful check on quality rather than a performance test, but there are probably many cases where design is limited by this property, especially at high temperatures. At present, tests have been made only at room temperature; but, no doubt, owing to self-heating under stress, the electric strength at high temperatures is an important factor in the test and so is taken into account so far as the comparison of the materials is concerned.

*Volume Resistivity.*—This was measured only incidentally and is considered of little importance for general purposes, especially as loss by conduction would be included in the loss measured in the power factor tests.

*Surface Deterioration in Sunlight.*—Surface stability in light is of considerable importance. The improvement most desired would be to make the material so that its surface resistivity never fell below, say  $10^{14}$  ohms, but, failing that, to retard the fall of resistance as much as possible. When the surface resistivity falls to about  $10^9$  ohms, as in all the cases under consideration, changes of a few parts per cent in the time of fall to a given value are of comparatively little importance and not worth great sacrifice in other directions, especially as the parts can often be shielded from light during service.

*Swelling in Oils.*—Freedom from swelling in saturated hydrocarbon oils, such as transformer oil, is of importance in certain applications, especially under hot conditions.

*Absorption of Water.*—Absorbed water is objectional owing to its well known deleterious effect on electrical properties; but it must be remembered that the effects on electrical properties do not necessarily vary in the same ratio as the amount of water absorbed, so too much importance should not be attached to minor variations in water absorption, which has only an indirect connection with the property of importance in service.

*Aging.*—Under ordinary atmospheric conditions and when shielded from bright light, hard rubber is acknowledged to be a highly stable material, but the possibility of deterioration at high temperatures may have to be taken into account in certain applications. The results indicate tentatively (1) the relative merits of the various materials under the actual conditions of test (in air at  $70^{\circ}\text{C}$ ), and (2) possibly, by analogy with soft rubber, their relative merits in resisting prolonged exposure to air at much lower temperatures. As with initial impact strength, more importance will be attached to the fall in strength of notched test-pieces than of unnotched pieces which are far superior and remain so even after aging.

## (ii) Choice of Best Composition and Vulcanization Time

The main results of the investigation are collected in the comprehensive Table 24 for easy reference. For the purpose of assessing the relative merits of the materials, the properties tested will be divided in the following discussion into two classes, major and minor properties; the former are properties in which improvement is most desired and which are of vital importance in design, while the latter are properties which are desirable, but which might be sacrificed in order to obtain optimum major properties. Further, some attempt has been made to indicate the influence of the variables in manufacture by a series of numbers to show at a glance the magnitude and direction of changes in

TABLE 24  
SUMMARY OF TESTS. PART I(a) RUBBER-SULFUR RATIO AND  
TIME OF VULCANIZATION

Nominal mixing (rubber-sulfur) Total sulfur by analysis		A (65/35) 35.25%					
Vulcanization (hrs. at 155° C)		3	3.75	5	7	10.5	
Chemical Properties							
Acetone extract (%)		7.81	6.03	4.99	4.83	4.94	
Combined sulfur (%)		28.8	30.4	31.4	31.6	31.5	
Free sulfur (%)		6.49	4.90	3.82	3.70	3.79	
Vulcanization coefficient		45.4	47.8	49.5	49.7	49.5	
General Properties							
Density at 15° C (g. per cc.)		1.195	1.198	1.199	1.200	1.201	
Cubical coefficient of expansion × 10 <sup>6</sup> (° C <sup>-1</sup> )		—	—	198	—	—	
Mechanical Properties							
Tensile	strength (kg. per sq. cm.)	742	771	793	813	782	
	ultimate elongation (%)	5.00	4.83	6.17	6.29	7.00	
	Young's modulus between 100 and 400 (kg. per sq. cm. in kg. per sq. cm.)	24600	26100	25000	25600	24600	
	resilient energy (kg. per sq. cm.)	26.6	25.6	35.3	37.0	40.8	
Cross-breaking	strength (kg. per sq. cm.)	1410	1470	1505	1530	1480	
	apparent breaking elonga- tion (%)	14.1	10.4	11.2	10.4	11.0	
Impact strength† (Method 2)	notched (kg.-cm. per sq. cm.)	3.6	2.05	2.0	1.7	1.75	
	unnotched (kg. cm. per sq. cm.)	40.0	55.5	55	46	46.5	
Plastic yield	Yield temperature (° C)	60.6	76.0	83.2	85.5	86.0	
	Yield in degrees of arc after 30 min. at	60° C	0.5	0.2	0.2	—	—
		70° C	5.9	0.4	0.2	—	0.2
		80° C	10.6	3.2	0.6	0.3	0.3
		90° C	12.2	10.9	5.6	5.0	4.5
		100° C	13.5	12.8	11.8	11.8	12.
Electrical Properties							
Permittivity at 1000 kc. per sec. at	20° C	2.80	2.82	2.86	2.88	—	
	40° C	—	—	—	—	—	
	60° C	2.87	2.86	2.91	2.90	—	
	75° C	—	—	—	—	—	
Power factor (%) at 1000 kc. per sec.) at	20° C	0.77	0.79	0.84	0.83	—	
	40° C	—	—	—	—	—	
	60° C	1.03	1.04	1.04	1.00	—	
	75° C	—	—	—	—	—	
Electric strength (kV per mm.§)		—	—	97.6	—	—	
Surface resistivity		(See Aging, below)					
Liquid absorption							
Water absorption (%) by volume	6.7 hrs.	0.38	—	0.39	—	0.38	
	6 days	0.51	—	0.48	—	0.44	

† See also initial impact strength results in aging investigation at end of table.

§ Vulcanization 2½, 4½, and 10 hours instead of 3, 5, and 10.5 hours.



TABLE 24—Continued

Nominal mixing (rubber-sulfur) Total sulfur by analysis		A (65/35) 35.25%					
Vulcanization (hrs. at 155° C)		3	3.75	5	7	10.5	
Swelling after 4000 hours (% by volume) in	petroleum ether	—	—	0.2—	—	—	
	paraffin	—	—	0.2—	—	—	
	transformer oil	—	—	0.2—	—	—	
Aging							
Surface deterioration	Initial apparent surface resistivity, ohms at 75% relative humidity ( $=20 \times p_r$ ) $\times 10^{-17}$	8.94	—	—	68.6	106	
	Time in standard	7.1	—	—	6.2	6.6	
	hours of day— light to fall to	10.3	—	—	8.7	9.1	
Nominal mixing (rubber-sulfur) Total sulfur by analysis		B (68/32) 32.35%					
Vulcanization (hrs. at 155° C)		3	3.75	5	7	10.5	
Chemical Properties							
Acetone extract (%)		5.91	4.12	3.26	2.87	2.85	
Combined sulfur (%)		27.8	29.7	30.8	30.8	30.8	
Free sulfur (%)		4.57	2.68	1.57	1.57	1.56	
Vulcanization coefficient		42.0	44.9	46.7	46.5	46.5	
General Properties							
Density at 15° C (g. per cc.)		1.172	1.174	1.176	1.177	1.177	
Cubical coefficient of expansion $\times 10^6$ (° C <sup>-1</sup> )		—	—	197	—	—	
Mechanical Properties							
Tensile	strength (kg. per sq. cm.)	716	753	755	767	753	
	ultimate elongation (%)	5.01	5.46	6.12	5.93	6.67	
	Young's modulus between 100 and 400 (kg. per sq. cm. in kg. per sq. cm.)	24800	24500	24000	24000	23900	
	resilient energy (kg. per sq. cm.)	25.4	29.3	33.6	32.2	37.0	
Cross-breaking	strength (kg. per sq. cm.)	1345	1420	1450	1460	1440	
	apparent breaking elongation (%)	16.2	12.3	11.3	11.5	11.9	
Impact strength† (Method 2)	notched (kg.-cm. per sq. cm.)	3.7	2.8	2.1	2.05	2.0	
	unnotched (kg.-cm. per sq. cm.)	33	60	56.5	59	56	
Plastic yield	Yield temperature (° C)	56.5	74.5	82.0	83.5	83.5	
	Yield in degrees of arc after 30 min. at	60° C	3.6	0.2	0.2	—	—
		70° C	10.8	0.6	0.3	0.3	0.2
		80° C	12.1	4.3	0.9	0.5	0.4
		90° C	13.3	11.6	6.4	5.9	5.6
		100° C	14.3	13.3	12.4	11.6	12.4
Electrical Properties							
Permittivity at 1000 kc. per sec. at	20° C	2.83	2.81	2.83	2.83	2.83	
	40° C	2.84	2.83	2.85	2.85	—	
	60° C	2.87	2.86	2.88	2.88	2.87	
	75° C	2.89	2.87	2.90	—	—	
Power factor (%) at 1000 kc. per sec.) at	20° C	0.78	0.86	0.88	0.87	0.90	
	40° C	0.87	0.96	1.00	0.98	—	
	60° C	1.11	1.06	1.10	1.07	1.11	
	75° C	1.63	1.18	1.17	—	—	

† See also initial impact strength results in aging investigation at end of table.



TABLE 24—Continued

Nominal mixing (rubber-sulfur) Total sulfur by analysis		B (68/32) 32.35%						
Vulcanization (hrs. at 155° C)		3	3.75	5	7	10.5		
Electric strength (kV per mm.§)		93.5	—	86.6	—	95.2		
Surface resistivity		(See Aging, below)						
Liquid Absorption								
Water absorption (% by volume)		{ 6.7 hrs.	0.38	—	0.39	—		
		{ 6 days	0.49	—	0.45	—		
Swelling after 4000 hours		{ petroleum ether	—	—	—	—		
(% by volume) in		{ paraffin	—	—	—	—		
		{ transformer oil	—	—	—	—		
Aging								
Surface deterioration	{ Initial apparent surface resistivity, ohms at 75% relative humidity ( $= 20 \times p_r \times 10^{-17}$ )	32.6	—	—	104	85.8		
		{ Time in standard	6.0	—	—	5.0	5.5	
			{ hours of day- $10^{16}$ ohms	9.3	—	—	7.1	8.1
				{ light to fall to $10^{12}$ ohms				
Nominal mixing (rubber-sulfur) Total sulfur by analysis		C (72/28) 28.30%						
Vulcanization (hrs. at 155° C)		3	3.75	5	7	10.5		
Chemical Properties								
Acetone extract (%)		4.09	2.62	2.07	2.01	1.89		
Combined sulfur (%)		25.8	27.2	27.8	28.0	28.0		
Free sulfur (%)		2.51	1.14	0.55	0.35	0.27		
Vulcanization coefficient		36.8	38.7	39.6	40.0	40.1		
General Properties								
Density at 15° C (g. per cc.)		1.142	1.145	1.147	1.147	1.148		
Cubical coefficient of expansion $\times 10^6$ (° C <sup>-1</sup> )		—	—	214	—	—		
Mechanical Properties								
Tensile	{ strength (kg. per sq. cm.)	633	712	692	721	694		
		{ ultimate elongation (%)	4.68	5.53	5.80	6.04	6.20	
		{ Young's modulus between 100 and 400 kg. per sq. cm. in (kg. per sq. cm.)	22300	24300	22100	22800	22200	
		{ resilient energy (kg. per sq. cm.)	20.9	28.3	29.1	31.9	31.5	
Cross-breaking	{ strength (kg. per sq. cm.)	1100*	1335	1350	1380	1335		
		{ apparent breaking elongation (%)	29.7*	15.2	14.1	13.4	13.3	
Impact strength (Method 2)	{ notched (kg.-cm. per sq. cm.)	4.0*	3.6	3.7	4.0	2.9		
		{ unnotched (kg.-cm. per sq. cm.)	66	70	75	72	61	
Plastic yield	{ Yield temperature (° C)	50.5	62.5	72.7	76.5	76.7		
		{ Yield in degrees of arc after 30 min. at	60° C	11.2	0.7	0.3	0.3	
			70° C	15.9	6.8	1.0	0.6	
			80° C	17.9	14.2	8.6	4.3	
			90° C	19.4	15.6	14.1	13.7	
			100° C	21.1	16.8	15.0	14.8	

§ Vulcanization 2½, 4½, and 10 hours instead of 3, 5, and 10.5 hours.

\* No sharp break. Cracked gradually on the underside.

TABLE 24—Continued

Nominal mixing (rubber-sulfur) Total sulfur bp analysis		C (72/28) 28.30%				
Vulcanization (hrs. at 155° C)		3	3.75	5	7	10.5
Electrical Properties						
Permittivity at 1000 kc. per sec. at	20° C	2.85	2.80	2.80	2.80	—
	40° C	—	—	—	—	—
	60° C	2.90	2.85	2.85	2.85	—
	75° C	—	—	—	—	—
Power factor (% at 1000 kc. per sec.) at	20° C	0.78	0.91	0.95	0.94	—
	40° C	—	—	—	—	—
	60° C	1.40	1.15	1.14	1.15	—
	75° C	—	—	—	—	—
Electric strength (kV per mm.)		—	—	109.3	—	—
Surface resistivity		(See Aging, below)				
Liquid Absorption						
Water absorption (% by volume)	6.7 hrs.	0.41	—	0.38	—	0.42
	6 days	0.54	—	0.46	—	0.48
Swelling after 4000 hours (% by volume) in						
	petroleum ether	—	approx. 10	—	—	—
	paraffin	—	0.5	—	—	—
	transformer oil	—	0.2	—	—	—
Aging						
Surface deterioration	Initial apparent surface resistivity, ohms at 75% relative humidity ( $=20 \times p_r \times 10^{-17}$ )	82.4	—	—	103	171
	Time in standard 10 <sup>12</sup> ohms	4.9	—	—	3.8	4.0
	hours of day—10 <sup>13</sup> ohms	7.6	—	—	6.1	6.2
	light to fall to					
Mixing (rubber-sulfur) Vulcanization (hrs. at 155° C)		K (65/35)				
		3	3.75	5	7	10.5
		L (70/30)				
		3	3.75	5	7	10.5
Change in impact strength on aging in air at 70° C	Initial impact strength (kg.-cm. per sq. cm.)					
	Notched	2.0	—	1.9	—	1.6
	Unnotched	43	—	42	—	46
	% change on 10 weeks' aging:					
	Notched	+25	—	+26	—	25
	Unnotched	+21	—	-40	—	-4

properties on varying the rubber-sulfur ratio and vulcanization time. The signs + and - are used to indicate improvement and deterioration, respectively. It is realized that such a system is arbitrary and depends on individual opinion and on the purpose for which a material is to be used, but it is hoped that its use may simplify the discussion of so many properties of varying importance.

#### Influence of Vulcanization Time

The influence of vulcanization time is shown in Table 25. The 5-hour vulcanization, after which practically no further combination of sulfur takes place, is used as a standard, and the changes due to shorter and longer times of

vulcanization are indicated as explained above. The mixings to which the results refer are indicated, where necessary, by letters in brackets.

(a) *Extension of Vulcanization Beyond 5 Hours*

There seems to be little change on continuing vulcanization to 7 hours. The increase in cross-breaking strength and tensile strength is negligible, though the increase of a few degrees in yield temperature might be worth obtaining for certain applications. It is interesting to note that some sort of vulcanization change continues without further combination of sulfur. On increasing the vulcanization from 7 to 10.5 hours, there are a few notable changes. There is a definite decrease in impact strength (notched) and an increase in tensile

TABLE 25  
CHANGES DUE TO VARIATION OF VULCANIZATION TIME FROM 5 HOURS

Property	3 hours	3.75 hours	7 hours	10.75 hours
<i>Major Properties</i>				
Cross-breaking and tensile strength	-2 (A & B) -3 (C)	-1	+1	0
Impact strength (notched)	+1 to +3 (A & B) 0 (C)	+2 (A & B) 0 (C)	0 +1	0 to -2 (A & B) -3 (C) +1
Plastic yield temperature	-3	-2	+1	+1
Power factor $\times$ permittivity (hot)	-3 (B & C)	0	0	0 (B)
Electric strength	+1 (Q)	—	—	+1 (Q)
Swelling in oil	—	-3 (C)*	—	—
Aging (notched sample)†	0 (K) -2 (L)	—	—	0
<i>Minor Properties</i>				
Free sulfur	-3	-2	0	0
Density	0	0	0	0
Coefficient of expansion	—	—	—	—
Cross-breaking elongation	+3	+1	0	0
Tensile elongation	-3	-2	0	+2
Resilient energy	-3	-2	0	+2
Young's modulus	0	0	0	0
Impact strength (unnotched)‡	+2 to -3	0	0	+1 to -2
Surface stability in daylight	+2	—	—	0
Absorption of water	0	—	—	0
Permittivity $\times$ power factor (cold)	+2	+1	0	0 (B)
Aging (unnotched sample)	+3 (K) +1 (L)	—	—	+3

\* Comparison between A, 5 hours, and C, 3.75 hours.

† Variation in opposite directions in two independent tests.

‡ All samples improved except L, 3 hours, which was practically unchanged.

elongation and resilient energy, which, however, is of doubtful value. The results are indefinite as to the change in impact strength (unnotched), but the tests indicate a considerable improvement in the maintenance of this property in air at 70° C. On the whole it is concluded that, pending confirmation of the aging effect, there is little to justify the extension of vulcanization beyond 5 hours with any mixing, especially as this would involve considerable extra cost in manufacture.

(v) *Reduction of Vulcanization Below 5 Hours*

The only major property which is substantially improved by undervulcanizing is impact strength (notched), but only in mixings A and B. Among

the minor properties there is some improvement in cross-breaking elongation, surface stability in daylight, loss factor (cold), and aging (unnotched samples and mixing K only). Against these are to be set losses with respect to cross-breaking and tensile strength, plastic yield temperature, loss factor (hot), free sulfur, tensile elongation, and resilient energy. Pending confirmation of the aging effect, it appears that the main object of vulcanizing for less than 5 hours would be to improve impact strength (notched), but that this would involve serious losses in other directions of which the most serious is plastic yield temperature. With mixings A and B, therefore, the choice of vulcanization time depends mainly on the relative importance of plastic yield and impact strength (notched). In these cases the highest impact strength and yield temperature cannot be obtained in the same material. On the other hand, with mixing C, there is very little to recommend undervulcanization since higher impact strength is not obtained thereby.

TABLE 26  
CHANGES DUE TO VARIATION OF RUBBER-SULFUR RATIO FROM 65/35

Property	(68/32)	(72/28)	(70/30)
<i>Major Properties</i>			
Cross-breaking and tensile strength	-2	-3	—
Impact strength (notched)	+1(+2 at 3.75 hrs.)	+3(+1 at 3 hrs.)	+2
Yield temperature	-1	-3	—
Loss factor (hot)	-1	-2(-3 at 3 hrs.)	—
Electric strength	-2	+2	—
Swelling*	—	-1	—
Aging (notched)	—	—	-1(5 & 10.5 hrs.) -2(3 hrs.)
<i>Minor Properties</i>			
Free sulfur	+2	+3	—
Density	0	+1	—
Coefficient of expansion	0	-1	—
Cross-breaking elongation	+1	+3	—
Tensile elongation	0	0	—
Resilient energy	0	-1	—
Young's modulus	-1	-2	—
Impact strength (unnotched)	+1	+3	+2
Surface stability	-2	-3	—
Water absorption	0	-1	—
Loss factor (cold)	-1	-2	—
Aging (unnotched)	—	—	-2

\* Comparison of C, 3.75 hours, and A, 5 hours.

#### Influence of Rubber-Sulfur Ratio

In a previous section of the report a distinction has been made between the 65/35 and 68/32 mixings, which have sufficient sulfur for the formation of a compound  $(C_5H_8)_n$ , and the 70/30 and 72/28 mixings in which the sulfur is not sufficient. Superficial examination of the results shows that in most respects 65/35 is superior to 68/32, so that in Table 26 all mixings will be compared with the 65/35.

#### (i) Choice between 65/35 and 68/32

There seems to be little to gain by adopting mixing 68/32 rather than 65/35. There is slight improvement in impact strength (notched and unnotched) and

cross-breaking elongation, and a considerable reduction in free sulfur. On the other hand, there are sacrifices to be made in respect of cross-breaking and tensile strength, modulus of elasticity, yield temperature, loss factor (hot and cold), electric strength, and surface stability in sunlight.

(ii) Choice Between 65/35 and 72/28

In a few important properties 72/28 is greatly preferable to 65/35. There is a great gain in impact strength (notched and unnotched), and cross-breaking elongation, a considerable gain in electric strength, a reduction in free sulfur, and a slight reduction in density. These gains, however, are obtained at a serious sacrifice in cross-breaking and tensile strength, yield temperature, loss factor (hot and cold), and surface stability in sunlight, with minor losses in respect of swelling in oils, coefficient of expansion, resilient energy, Young's modulus, and water absorption. No information is available on aging, but one would expect from the results obtained with the 70/30 mixing L that 72/28 would be inferior to 65/35 in this also, so the initial superiority in impact strength would be lost under certain conditions.

(iii) Choice Between 65/35 and 70/30

There is insufficient information to decide on the desirability of the 70/30 mixing L as a compromise, except by interpolation between the results of B and C.

It will be seen that the advantages and disadvantages of using a low-sulfur mixing are very similar to those of using an undervulcanized high-sulfur mixing, namely that a high impact strength (notched) is gained at the cost of a serious loss in yield temperature. This is not true in all respects, as will be seen from Table 27, in which the changes due to (1) undervulcanization of mixing A

TABLE 27  
COMPARISON OF SHORT VULCANIZATION AND LOW SULFUR  
AS MEANS OF CHANGING PROPERTIES

Property	(a) A, 3 hrs. compared with A, 5 hrs.	(b) C, 5 hrs. compared with A, 5 hrs.
<i>Major Properties</i>		
Cross-breaking and tensile strength	-2	-3
Impact strength (notched)	+1 to +3	+3
Yield temperature	-3	-3
Loss factor (hot)	-3	-2
Electric strength	—	+2 (P and R)
Swelling	—	—
Aging (notched)	0	—
<i>Minor Properties</i>		
Free sulfur	-3	+3
Density	0	+1
Coefficient of expansion	—	-1
Cross-breaking elongation	+3	+3
Tensile elongation	-3	0
Resilient energy	-3	-1
Young's modulus	0	-3
Impact strength (unnotched)	+2 to -3	+3
Surface stability	+2	-3
Water absorption	0	-1
Loss factor (cold)	+2	-2
Aging (unnotched)	+3 (K)	—

(3 hours instead of 5 hours) are compared with those due to (2) reduction of sulfur to that of mixing C (72/28 instead of 65/35) without change of vulcanization time from 5 hours.

In all the major properties, the influence of these two variables appears to be qualitatively similar. Among some of the minor properties the influence is in opposite directions. Thus, undercure of A involves disadvantages with respect to free sulfur and impact strength (unnotched), and advantages with respect to surface stability, loss factor (cold), and aging (unnotched), whereas the changes in these properties due to reduction of sulfur are in the opposite directions. Also, undercure involves a great loss in tensile elongation and resilient energy, and reduction of sulfur a greater loss in Young's modulus. The quantitative comparison of the influence of undercure and reduction of sulfur may be seen in Table 28 where values are given in most cases by reading from smooth curves. The comparison which has been made is between two materials of approximately equal impact strength (notched).

TABLE 28  
QUANTITATIVE COMPARISON BETWEEN A, 3 HOURS, AND C, 5 HOURS

Property	A, 3 hours	C, 5 hours	Unit
<i>Major Properties</i>			
Cross-breaking and tensile strength	1410	1360	kg. per sq. cm.
Impact strength (notched)	3.6	3.7	kg.-cm. per sq. cm.
Yield temperature	60.6	72.7	°C
Loss factor (hot)	1.03	1.14	%
Electric strength	—	109.3 (R)	kV per mm.
Swelling	—	0.5 (paraffin)	% by volume
Aging (notched)	+25 (K)	—	%
<i>Minor Properties</i>			
Free sulfur	6.5	0.55	%
Density	1.195	1.147	g. per cc.
Coefficient of expansion	—	214	per °C × 10 <sup>6</sup>
Cross-breaking elongation	14	14	%
Tensile elongation	5	6	%
Resilient energy	26.2	28.5	kg.-cm. per cc.
Young's modulus	24600	22500	kg. per sq. cm.
Impact strength (unnotched)	40	40	kg.-cm. per sq. cm.
Surface stability	10.3	6.1	hrs. to fall to 10 <sup>12</sup> ohms
Water absorption	0.38	0.38	%
Loss factor (cold)	0.77	0.95	%
Aging (unnotched)	+21 (K)	—	%

As a means of increasing impact strength without serious loss in yield temperature, reduction of total sulfur is greatly superior to undercure. For equal impact strengths (notched), C is superior in impact strength (unnotched), yield temperature, and freedom from uncombined sulfur, but at some sacrifice in loss factor (hot and cold) and surface stability. In view of the connection found between yield temperature and increase of power factor with temperature, it seems probable that A, 3 hours, would lose its superiority in loss factor (hot) on raising the temperature to 70 or 80° C.

The adoption of a fully vulcanized low-sulfur mixing instead of an undercure high-sulfur mixing has one notable advantage from the manufacturing standpoint. At about 3 hours' vulcanization at 155° C, both impact strength and yield temperature are very sensitive to vulcanization time at a



fixed temperature and, therefore, also to temperature of vulcanization at a fixed vulcanization time. The repetition of an undervulcanized material therefore requires much more accurate control of temperature and every other factor, such as source of raw rubber, which affects the rate of vulcanization.

### General Conclusions

On the whole, although selection for special purposes might have to be made from several of the materials investigated, most general purposes would be covered by one high-sulfur and one low-sulfur mixing, in each case just fully vulcanized, *i.e.*, until combination of sulfur had practically ceased.

### B. CORRELATION BETWEEN VARIOUS PROPERTIES

Many of the properties tested are selected as performance properties of practical interest rather than as fundamental properties. It is of some practical and theoretical value to consider briefly the content to which these properties depend on one another or are determined by common factors in the materials examined.

#### (i) Tensile Strength and Cross-Breaking Strength

It has already been noted that tensile strength as determined directly and as calculated on the usual assumptions from cross-breaking tests differ in the ratio of nearly two to one. Nevertheless, the two properties seem to vary in nearly constant ratio. This is perhaps due to the similarity of form of the tensile stress-strain curve for all mixings and vulcanization time. Similarity of compression curves also would be necessary to account for the observation, but no evidence on this point is available. The constance of ratio cannot be assumed as universally applicable to all hard rubbers, but it appears unnecessary to duplicate the cross-breaking test by the more troublesome tensile test in comparing the similar types of material.

#### (ii) Impact Strength and Other Mechanical Properties

Since impact strengths, notched and unnotched, appear to involve different complexes of properties, they must be considered separately.

(a) *Impact Strength (unnotched).*—Although, no doubt, tensile strength is an important factor in impact strength, the two properties are not simply related (cross-breaking strength need not be considered separately since it is proportional to tensile strength). When the time of vulcanization is varied, both tensile strength and impact strength show a maximum with medium times, but the tensile strength maximum is not so sharp. When the rubber-sulfur ratio is varied, the materials are definitely in opposite orders of merit with respect to the two properties.

"Resilient energy", or the work done in stretching unit volume to the breaking point, was measured with a view to correlating it with impact strength, but it does not vary simply with the latter when either vulcanization time or rubber-sulfur ratio is varied. This is probably due largely to the different types of stress imposed (tensile and three-point loading) in the two tests. Resilient energy and impact strength improved up to about 5 hours' vulcanization, after which the former continues to increase while the latter decreases. Moreover, when rubber-sulfur ratio is varied, the two properties are affected in different directions.

The value of the "resilient energy" involved in straining to the breaking

point in a cross-breaking test is not available, since the complete stress-strain curve was not determined. Changes in this property may, however, be indicated qualitatively by the product of cross-breaking strength and "elongation". This product agrees with impact strength as to the superiority of mixing C over A and B, but does not reproduce the maximum at 5 hours' vulcanization, there being a rapid reduction in the product from 3 to 3.75 hours.

(b) *Impact Strength (notched).*—Neither tensile strength nor tensile resilient energy corresponds to impact strength (notched) in its variation with the time of vulcanization and rubber-sulfur ratio. C is superior to A and B in impact strength, whereas A, B, and C are in descending order of merit in the former two properties. When vulcanization time is increased, impact strength decreases, tensile strength passes through a maximum and resilient energy increases. Variations of impact strength and of the product of cross-breaking strength and "elongation" follow one another closely enough to justify further attention to this relation in future work. Since the types of stress are more similar in these two tests, it is suggested that complete stress-strain curves should be obtained in future cross-breaking tests so that the total work required to break the sample can be calculated. It has already been found that high impact strength (notched) and high yield temperature appear to be incompatible. Impact strength decreases with increasing vulcanization and with increasing total sulfur, whereas yield temperature varies in the opposite direction in both cases. Observations recorded here and elsewhere suggest that there is a fundamental connection between the two properties depending on some feature of the structure of hard rubber. If impact strength is plotted against yield temperature the correlation is not accurate, but in view of the uncertainties connected with impact strength, it is sufficiently striking to justify further study of the relation.

### (iii) Electric Strength and Loss Factor

There is little evidence of a simple connection between electric strength at a frequency of 50 cycles per second and loss factor at 100 kc. per second. Mixing C has a higher electric strength than B in spite of a high loss factor at both 20° C and 60° C and probably a tendency to rapidly increasing dielectric loss at a higher temperature. The minima of electric strength with both vulcanization time (mixing B) and rubber-sulfur ratio (5 hours) are not explained by variations in loss factor which do not show corresponding maxima or minima.

### (iv) Aging Changes

The rapid aging of hard rubbers vulcanized for 5 hours compared with that of under- and overvulcanized materials was unexpected, and it would be premature to attempt an explanation in the absence of confirmation and of further knowledge as to the chemical and physical changes which occur on continued vulcanization. The effect cannot be attributed to accidental errors of measurement, since it is consistent in two mixings and in a number of tests after various aging periods. There is, however, the possibility of unsuspected variables in the preparation of the sheets or test-pieces. It may be noted in this connection that there is a similar maximum rate of deterioration in sunlight when vulcanization time is varied and that the high-sulfur mixing is superior both in sunlight and in air at 70° C. It has been suggested by several commentators that the deterioration of the surface in sunlight is due to changes in the uncombined sulfur, although it has been shown in researches by the

R.A.B.R.M.<sup>5</sup> that the sulfuric acid is derived from the combined sulfur of the hydrocarbon-sulfur nucleus. The latter observation is supported by the fact that the deterioration in the present samples is less rapid the higher the total percentage of sulfur in the mixing and is least rapid with the least vulcanized samples. It will be seen that in both cases the reduction of free sulfur is accompanied by an increase in the rate of deterioration. For example, the extreme cases A, 3 hours, and C, 7 hours, may be pointed out, in which the free sulfur percentages are 6.5 and 0.35, respectively, and the times for the surface resistivity to fall to  $10^{12}$  ohms, are 10.3 and 6.1 hours respectively.

#### C. BEARING OF RESULTS ON SPECIFICATIONS FOR EBONITE

It is not one of the objects of this work to make positive proposals as to specifications. The materials examined are composed of rubber and sulfur only, whereas many commercial materials of good quality and substantially unloaded contain ingredients such as high-grade ebonite dust, accelerators, activators, softeners and the like. It can readily be seen, however, that there are dangers involved in certain types of specification even if the materials admitted are of rubber and sulfur only, and it may be assumed that the question would be greatly complicated if more ingredients were allowed.

In many early specifications, attempts were made to decide on the best composition and method of manufacture, and then specify sufficient chemical and physical tests to ensure the correct manufacture. In contrast to this, the modern tendency is to devise the minimum number of performance tests which will ensure satisfactory service and leave the manufacturer the greatest possible liberty as to the means of making his material to pass these tests. In practice, the latter method often cannot be carried to its logical conclusion without serious multiplication of tests, the result being a compromise involving the principal performance tests and some compositional tests to prevent any great departure from what is generally acknowledged to be good practice.

These considerations are illustrated by the development of British Standard Specification No. 234. In the 1925 issue, which was based on an earlier General Post Office Specification, total sulfur was limited to 30 per cent, free sulfur to 5 per cent, organic acetone extract to 10 per cent, and ash to 3 per cent. The only mechanical test was a cantilever cross-breaking test. The object of limiting the total sulfur was presumably to restrict the vulcanization coefficient and so avoid brittleness, but this limitation by itself was insufficient, for the rubber hydrocarbon might have been as low as 57 per cent, giving a possible vulcanization coefficient of 53, without failing under the chemical tests. It may, of course, have been impossible with the allowed high percentages of non-hydrocarbon materials to pass the electrical and mechanical tests, but the chemical requirements were indefinite in that the sulfur was calculated on the whole mixing. This was corrected in the 1931 issue by calculating the permissible combined sulfur on the residue after subtraction of all but rubber and combined sulfur, *i.e.*, in effect by specifying the approximate vulcanization coefficient. Although a plastic yield test was considered, it was contended that it was unnecessary, since it was not possible to meet the mechanical and electrical requirements with a material which was unsatisfactory in that respect. In the 1933 issue of the specification a further development has been made by leaving the total sulfur unrestricted, but limiting the free sulfur to a lower percentage. The question now arises whether there are sufficient tests to ensure good performance in properties not now specified, particularly impact strength, plastic yield temperature, and aging.

It will be clear from the present work, even if there were any doubt previously, that these important properties are not determinable from a single chemical property, such as vulcanization coefficient. If the material were known to be made from new rubber and sulfur only and the rubber-sulfur ratio were fixed, the vulcanization coefficient might be of some value for the purpose of indicating the degree of vulcanization; but it has been shown that when the rubber-sulfur ratio is variable, plastic yield temperature and impact strength are not simply related to vulcanization coefficient, the former being more closely associated with the difference between the actual coefficient and that obtainable on prolonged vulcanization; and even that relation only holds with high-sulfur materials. Moreover, if a high-grade dust were to be used, the problem would be still more complicated, since the quantity of dust could not be estimated quantitatively and the distribution of combined sulfur between the dust and the remainder could not be determined. To some extent it is true that a low vulcanization coefficient favors a high impact strength (notched), whether due to a low total sulfur content or to undervulcanization, but the relation is not sufficiently definite for specification purposes. In the case of plastic yield temperature it is seen that a vulcanization coefficient which gives a good performance with mixing C permits an intolerably low yield temperature with B and a still lower one with A.

It is equally clear that the specification of a minimum cross-breaking strength is not sufficient to ensure a good impact strength, for the two properties vary in opposite directions with rubber-sulfur ratio, and over part of the range, with vulcanization time. Also, the relation between yield temperature and cross-breaking strength is not sufficiently definite for the latter only to be specified. For example, if cross-breaking strength were fixed at 1350 kg. per sq. cm. to permit the use of mixing C vulcanized for 5 hours having a yield temperature of 72.7° C, the cross-breaking strength test could then be passed by mixing A vulcanized for less than 3 hours and having a yield temperature much less than 60° C. The position in regard to aging is indefinite, and there appears to be no way of ensuring good aging properties except by a direct performance test.

It has been shown that the best properties cannot be combined in a single material within the present range of composition, so there must be some compromise in drawing up any specification for hard rubber so as to obtain good all-round performance. It may be advisable, however, at a later stage to consider variations for special purposes. For example, for some purposes the requirements as to impact strength may have to be made severe, in which case there would have to be some relaxation of the demands on cross-breaking strength, yield temperature, loss factor, surface stability in sunlight, and aging in air at high temperatures. Similarly an attempt to secure the best possible yield temperature would involve some sacrifice in impact strength and other properties.

#### D. RECOMMENDATIONS FOR FURTHER WORK

##### (i) Study of Definite Properties

During the discussion of the above experimental work it appears that certain questions concerning the relative merits of the various materials should receive further study before this section of the work is considered complete. These are briefly enumerated below.

(a) Conditions under which free sulfur may cause corrosion of metal parts, and percentage of free sulfur permissible.

(b) Relative merits of the materials in withstanding high electric stresses at high frequencies.

(c) Absorption of transformer oil and other liquids used in conjunction with hard rubber at high temperatures, and more complete study of the influence of rubber-sulfur ratio and vulcanization time.

(d) Plastic yield characteristics under low stresses and longer periods of stress, and their correspondence with the results under the present conditions of test.

(e) Factors in the preparation of hard rubber and of test-pieces therefrom which cause variability in impact and aging test results, and confirmation of results reported above.

(f) Confirmation of influence of rubber-sulfur ratio and vulcanization time on electric strength.

## (ii) Fundamental Research

It is recommended also that the present systematic investigation should be supplemented by a more fundamental study of the chemical and physical structure of hard rubber. The present work suggests at least three different fields of research, the results of which should serve to direct the systematic investigation into the most hopeful directions.

(a) As is known, the end product of the combination of rubber and sulfur is not a simple product  $(C_5H_8S)_n$ , but is complicated by the formation of substitution instead of addition products and of compounds of sulfur with nonrubber components of the rubber. An understanding of these complex reactions would no doubt throw light on surface deterioration in sunlight, aging in air of high temperatures, the incompleteness of correlation between vulcanization coefficient and physical properties, changes in plastic properties on continued vulcanization after combination of sulfur has ceased, and the great decrease in absorption of oil in the last stages of combination of sulfur.

(b) The physical structure of hard rubber has already been studied through the property of plastic yield and resembles in many respects a two-phase structure having a transition temperature, continuously variable with percentage of combined sulfur, at which one phase becomes fluid, the other remaining elastic. This change is accompanied by marked changes in dielectric loss and coefficient of expansion. There also seems to be an intimate connection between impact strength and the transition temperature. Further study of the physical structure by means of these properties offers another promising line of inquiry.

(c) There is still uncertainty as to the combination of physical properties involved in tensile, cross-breaking, and impact fractures. Some rational theory of the process of fracture in each case would be of great help in interpreting results of tests and in planning future work. Such a theory would be of general interest in connection with other insulating materials than hard rubber.

## REFERENCES

<sup>1</sup> Dunton and Muir, *Electrician* 104, 326 (1930).

<sup>2</sup> *J. Rubber Research* 12, 133 (1943).

<sup>3</sup> *J. Rubber Research* 15, 134 (1946).

<sup>4</sup> Dieterich and Gray, *Ind. Eng. Chem.* 18, 428 (1926).

<sup>5</sup> Fry and Porritt, *India-Rubber J.* 78, 307 (1929); Webster and Porritt, *India-Rubber J.* 79, 239 (1930).



# PROPERTIES OF HARD RUBBER. XVIII. ACTION OF HYDROCARBON OILS AT HIGH TEMPERATURES (PART XV OF SWELLING OF RUBBER)

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It has already been shown<sup>1</sup> that liquids consisting essentially of aliphatic hydrocarbons, *e.g.*, petroleum ether, paraffin, and transformer oil, had practically no swelling action at 34° C on two samples of hard rubber composed of rubber and sulfur only.

Hard rubber shows a pronounced change in properties at temperatures above a critical value ("yield temperature") in the neighborhood of 50°–80° C, the most noticeable effect being that it becomes much softer and more susceptible to plastic flow. It seemed likely, therefore, that the swelling action of liquids such as those mentioned above might be much greater at temperatures above this critical value. This view was strengthened by the statement of Duntun and Muir<sup>2</sup> that hard rubber is "badly attacked" by immersion for 7 days in "hot" transformer oil.

As no data appear to have been published on the effect of temperature on the swelling of hard rubber, experiments were made to examine this effect. Details of the hard rubber samples used are as follows<sup>3</sup>.

Sample	Composition rubber : sulfur	Time of vulcanization at 155° C	Combined sulfur (%)	Yield temperature*
A3	65:35	3 hours	28.8	60° C
B3	68:32	3 hours	27.8	50
C3	72:28	3 hours	25.8	45
C3 <sub>1</sub>	72:28	3.75 hours	27.2	60

\* Approximate temperature at which plastic flow begins to increase rapidly; this is not exactly equal to the yield temperature as defined in Part XVI.

Specimens of each of these materials were immersed in paraffin lamp oil and in transformer oil; these were the same samples as used in previous experiments and had the following characteristics:

Paraffin: boiling range 180°–280° C; density at 21° C (70° F) 0.803.

Transformer oil: viscosity (at 21° C) 37 cp.; density at 21° C (70° F) 0.860.

In each case experiments were made at two temperatures, 20° and 70° C; as very little swelling occurred after 29 days at 70° C, the temperature in these experiments was thereafter raised to 100° C. Even 70° C is well above the yield temperature of the samples, so that any change in swelling due to the changes in the physical properties of the material above this temperature should be well displayed. The bottles containing the liquids and test-pieces (1.9 cm. square by 0.5 cm. thick) were kept in darkness in thermostats, and from time to time the test-pieces were removed, dried, and weighed to determine the change in weight due to immersion in the liquid.

\* Reprinted from the *Journal of Rubber Research*, Vol. 15, No. 8, pages 179–180, August 1946.



In view of the very small changes in weight observed and the fact that many of these were negative, there was no point in converting the results into change in volume as is usual in swelling tests; the results are therefore given simply as percentage change in weight (see Table 1).

In the case of paraffin, although there is a measurable absorption of liquid at the higher temperature, this is very small compared with the amount absorbed by soft vulcanized rubber, which ranges from about 100 to 300 per cent (by volume) at ordinary temperature. The swelling is less the higher the combined sulfur content, in accordance with previous observations on the swelling of hard rubber<sup>1</sup>.

TABLE 1

Liquid	Sample and temperature*	Percentage change in weight† after immersion for				
		1 day	7 days	29 days	32 days	67 days
Paraffin	A2 20° C	-0.05	-0.1	-0.1	—	-0.05
	70-100°	0.05	0.2	0.35	0.6	0.8
	B3 20° C	-0.05	-0.1	-0.1	—	-0.05
	70-100°	0.2	0.5	0.9	1.45	1.85
	C3 20° C	-0.05	-0.05	-0.05	—	0.0
	70-100°	0.95	2.8	3.8	4.25	4.55
	C3½ 20° C	0.0	-0.05	-0.05	—	0.0
	70-100°	0.45	1.3	2.1	2.9	3.9
Transformer oil	A3 20° C	0.0	0.0	0.0	—	0.0
	70-100°	-0.1	-0.15	-0.25	-0.25	-0.25
	B3 20° C	-0.05	-0.05	-0.1	—	0.0
	70-100°	-0.1	-0.25	-0.25	-0.35	-0.3
	C3 20° C	0.0	-0.05	-0.1	—	0.0
	70-100°	0.0	-0.2	-0.2	-0.3	-0.15
	C3½ 20° C	-0.05	-0.05	-0.15	—	0.0
	70-100°	-0.05	-0.25	-0.25	-0.3	-0.05

\* In the 70-100° C experiments the temperature was 70° C up to 29 days and 100° C after this.

† Increase unless marked minus.

Transformer oil, at either low or high temperature, produces no effect beyond a trifling decrease in weight, evidently due to a slight solvent action on the hard rubber or the free sulfur or resins. This effect is greater at the higher temperature, as might be expected.

From these experiments it may be concluded that rubber-sulfur ebonites containing 25.8 per cent or more of combined sulfur are very little affected by prolonged exposure to paraffin or transformer oil at temperatures up to 100° C. This conclusion may appear to be at variance with the statement of Dunton and Muir<sup>2</sup> quoted above, but it is probable that the hard rubber mentioned by them was very different from those examined in the present experiments, and their expression "hot" used with reference to the oil may have denoted a higher temperature than 100° C.

#### REFERENCES

<sup>1</sup> Parris and Scott, *J. Rubber Research* 10, 123 (1941).

<sup>2</sup> Dunton and Muir, *Electrician* 104, 326 (1930).

\*The combined sulfur and yield temperature values are from Parts XV and XVI (Church and Daynes, *J. Rubber Research* 14, 165 (1945); 15, 127 (1946)).

# THE VULCANIZATION OF RUBBER WITH PHENOL-FORMALDEHYDE DERIVATIVES. INAPPLICABILITY OF THE CHROMANE THEORY \*

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The chemistry of phenol-formaldehyde resins has developed enormously since 1938. Zinke, von Euler and Hultzsche in particular have enlarged our knowledge about the constitution of resols and resites by their investigations in the complicated field of resol hardening. In addition, reactions between hydroxyphenols and unsaturated compounds have been studied. Hultzsche<sup>1</sup> proved the formation of a chromane ring system by heating an unsaturated hydrocarbon with a hydroxyphenol. Later Greth<sup>2</sup> described the reaction between resols and fat oils as an analogous one, also in these cases supposing the formation of chromane derivatives. According to the latter two main reactions lead to the formation of macromolecular compounds:

- (1) the formation of chromane rings between the resol and the unsaturated compound;
- (2) the formation of intermolecular oxygen bonds between the methoxy groups of the hydroxyphenols and resols.

It seemed reasonable to explain the vulcanization of rubber with resols and dihydroxyphenols by this chromane theory. However, it is necessary first of all to have a clear idea of the various possibilities which may be involved. Only after this will it be possible to decide whether the chromane theory may be applied to vulcanization with phenol-formaldehyde derivatives<sup>3</sup> as well.

## *Vulcanization according to the chromane theory.*

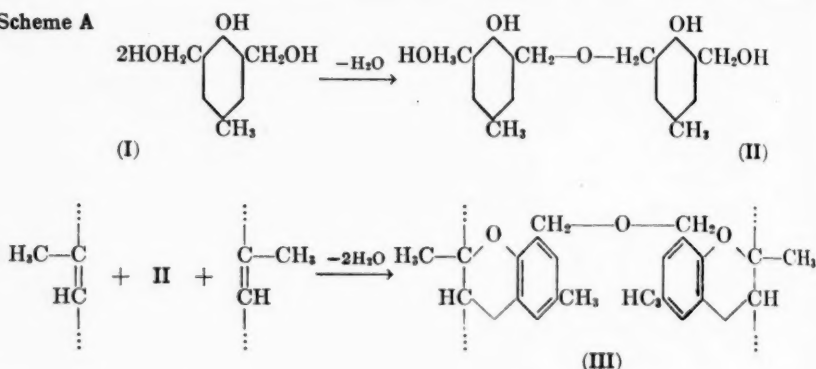
Choosing 2,6-dihydroxymethyl-*p*-cresol<sup>4</sup> as an example, we may formulate the vulcanization process according to the chromane theory in three different ways, as indicated in Figure 1.

First of all it is important to examine whether or not these three possibilities are equivalent. According to Scheme C, one molecule of rubber combines with one molecule of 2,6-dihydroxymethyl-*p*-cresol (I) to form the chromane derivative, IV; subsequently two molecules of the latter combine to form the vulcanizate, III, with liberation of water. The scheme shows that this liberation of water should occur between two molecules of a hydroxyphenol derivative, in which the phenolic hydroxyl group is masked in the chromane ring. This reaction is highly improbable, for such liberation of water is characteristic only of hydroxyphenols which possess unsubstituted phenolic hydroxyl groups. Hence scheme C has to be disregarded.

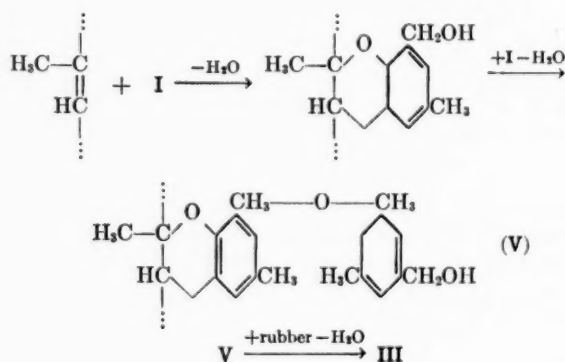
\* Communication No. 44 of the Rubber-Stichting, Delft, Holland.

Scheme B starts in the same manner as does C; subsequently the chromane derivative, IV, combines with another molecule of 2,6-dihydroxymethyl-*p*-cresol (I) to form the compound V, the latter combining in turn with another molecule of rubber to form the vulcanizate III. The main difficulty of this scheme is the formation of compound V, for this is based on a reaction between 2,6-dihydroxymethyl-*p*-cresol (I) and an aromatic alcohol (IV). However, our own experimental results have shown that resols and dihydroxyphenols do not generally

## Scheme A



## Scheme B



## Scheme C

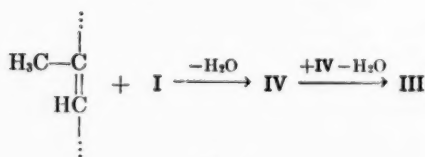


Fig. 1.

combine with alcohols on heating at about 100° C. Although the vulcanization temperature of 2,6-dihydroxymethyl-*p*-cresol is much higher (155° C), the reaction mentioned proceeds only to a minor degree. The reactions of Scheme B must, therefore, be considered to be of minor importance.

Scheme A is based on the formation of a resol (II) from the dihydroxyphenol (I), this resol subsequently uniting two molecules of rubber by the formation of chromane rings. From the foregoing it appears clear that this manner of

formulating the chromane theory of vulcanization must be regarded as the most probable. There are, however, certain objections against it.

*Objections to the chromane theory.*

Supposing the chromane theory to be correct, the dihydroxyphenols<sup>5</sup>, VI and VII, might be expected to have a much stronger tendency to vulcanize 2,6-dihydroxymethyl-*p*-cresol (I).

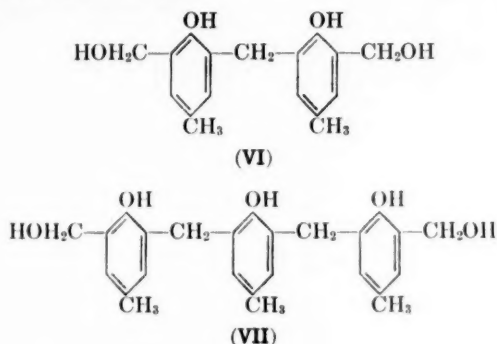


FIG. 2.

In fact these two compounds can immediately and entirely take part in the formation of a vulcanizate, whereas 2,6-dihydroxymethyl-*p*-cresol partly disappears in compound IV, the latter not being important in the vulcanization. This supposition is not correct, as can be seen from Table 1.

It is obvious that vulcanizates obtained with compounds VI and VII do not have superior mechanical properties<sup>6</sup>.

A second objection to the chromane theory is the great speed of the vulcanization reaction of the pseudo-phenol halides. In vulcanizing with di-

TABLE 1  
MECHANICAL PROPERTIES OF VULCANIZATES OF 100 PARTS OF RUBBER AND 40 PARTS  
OF THE DIHYDROXYPHENOLS I, VI AND VII, RESPECTIVELY.  
VULCANIZATION: 2 HOURS AND 155° C.

	I	VI	VII
Tensile strength (kg. per sq. cm.)	159	36	162
Elongation at break (percentage)	513	152	438
Modulus at 100% (kg. per sq. cm.)	10	25	21
Modulus at 200% (kg. per sq. cm.)	20	—	44
Modulus at 400% (kg. per sq. cm.)	82	—	128
Hardness (Shore)	45	55	52

hydroxyphenols, a reaction time of 2 hours and a temperature of about 155° C are required; in the case of pseudo-phenol halides only a few minutes at a much lower temperature are sufficient. The results of vulcanization with several of these compounds are collected in table 2.

If vulcanization with these halogen compounds takes place in a similar way to that shown by scheme A, the first stage would be the formation of the larger compound IX, formed from at least two molecules of the vulcanizing agent (VIII). Figure 3 represents this reaction with 2,6- bromomethyl-*p*-cresol (VIII) as an example.

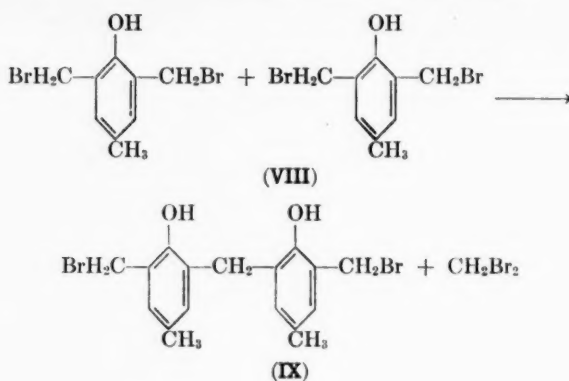


FIG. 3.

A reaction of this kind would have to take place by liberation of a compound  $\text{CH}_2\text{X}_2$ , in which X is a halogen. But this liberation does not occur sufficiently rapidly to explain the vulcanization in this way. In fact, as can be seen from Table 2, it is possible to vulcanize with 2,6-dibromomethyl-*p*-cresol in 15 minutes at  $100^\circ\text{C}$ , whereas in the pure state the substance is perfectly stable when heated for the same time at that temperature. Consequently it seems far more probable that these pseudo-phenol halides vulcanize without liberation of  $\text{CH}_2\text{X}_2$ . A third objection to scheme A arises if we try to explain in

TABLE 2  
MECHANICAL PROPERTIES OF VULCANIZATES OF RUBBER AND SEVERAL  
PSEUDO-PHENOL HALIDES.

Rubber	parts by weight	100	100	100	100
2,6-Dichloromethyl- <i>p</i> -cresol <sup>7</sup>	parts by weight	10	40	—	—
2,6-Dibromomethyl- <i>p</i> -cresol <sup>8</sup>	parts by weight	—	—	10	40
Vulcanization time	minutes	25	15	30	15
Vulcanization temperature	$^\circ\text{C}$	120	100	125	100
Tensile strength	kg. per sq. cm.	68	17	90	20
Elongation at break	percentage	563	107	695	193
Modulus at 100%	kg. per sq. cm.	6	16	3	11
Modulus at 200%	kg. per sq. cm.	9	—	6	—
Modulus at 400%	kg. per sq. cm.	24	—	16	—
Hardness	Shore	30	50	30	45

this way the reaction mechanism of vulcanization with 2,6-dihydroxymethyl-*o*-cresol<sup>9</sup> (X). In this case the resol first formed must possess the structure indicated by XI, for only then is a repeated formation of chromane rings possible, in virtue of the *ortho*-positions of the two alcoholic groups with respect to the phenolic hydroxyl groups.

Compounds of the type XII, which have only one alcoholic group in the *ortho*-position, might in consequence react with only one molecule of rubber; a similar reaction with compounds of the type XIII is entirely impossible. Hence the vulcanization reaction according to the chromane theory cannot be explained by either of these compounds.

Now the primary formation of the resol complex XI, which is necessary for vulcanization from this point of view, is based on the supposition that the

reactivity of the *para* alcoholic group of 2,6-dihydroxymethyl-*o*-cresol is greater than, or at least as great as, that of the *ortho* alcoholic group. If this is correct, 2,6-dihydroxymethyl-*p*-cresol, which contains only the slower *ortho* alcoholic groups, should require a vulcanization temperature higher than, or at least as, high as that of 2,6-dihydroxymethyl-*o*-cresol. Our experimental results, however, do not support this idea.

2,6-Dihydroxymethyl-*p*-cresol vulcanizes very well at a temperature of 155° C; 2,6-dihydroxymethyl-*o*-cresol on the other hand requires a temperature of about 200° C. Another indication that the *ortho*-alcoholic group has the greater reactivity is the fact that 2,6-dihydroxymethyl-*o*-cresol in mixtures with 2,6-dihydroxymethyl-*p*-cresol diminishes greatly the vulcanizing power of the latter at 155° C by blocking the alcoholic groups.

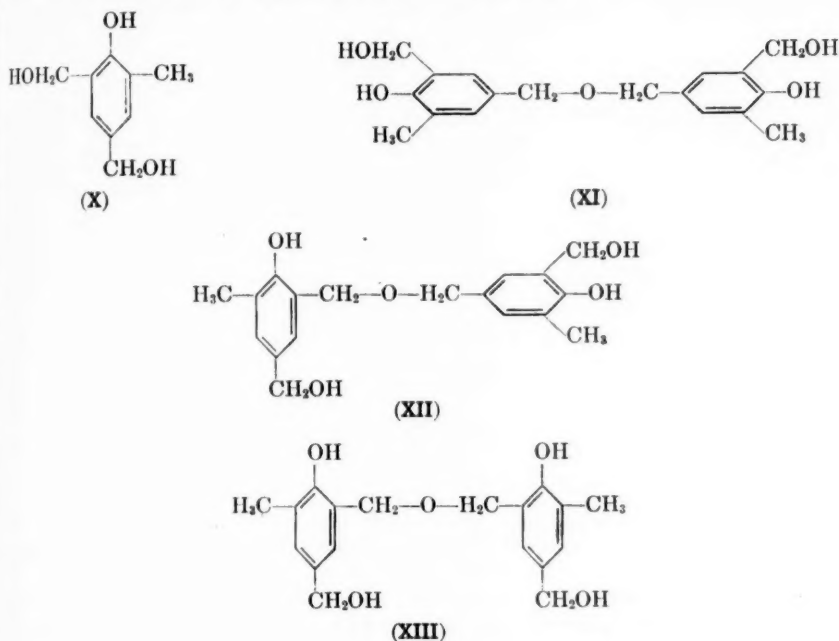


FIG. 4.

Table 3 shows the mechanical properties of some vulcanizates obtained with 2,6-dihydroxymethyl-*p*-cresol, 2,6-dihydroxymethyl-*o*-cresol, and mixtures of these two.

From these considerations it follows that the formation of compounds of type XIII, and possibly also XII, by the more reactive *ortho*-alcoholic groups, is the more likely. But as two chromane rings cannot be formed by such compounds, it is impossible to explain in this way the mechanism of vulcanization with 2,6-dihydroxymethyl-*o*-cresol.

In view of all this it was important to carry out vulcanization experiments directly with compounds of type XIII, for positive results would be an indication that vulcanization can take place without the formation of chromane rings. So the attempt was made to prepare a dihydroxyphenol with its two alcoholic groups in the *para*-position with respect to the phenolic hydroxyl groups.



TABLE 3

MECHANICAL PROPERTIES OF VULCANIZATES, OBTAINED WITH 2,6-DIHYDROXYMETHYL-*p*-CRESOL, 2,6-DIHYDROXYMETHYL-*o*-CRESOL, AND WITH MIXTURES OF THE TWO  
(Vulcanization time 2 hours)

Rubber	parts by weight	100	100	100	100	100	100	100
2,6-Dihydroxymethyl- <i>p</i> -cresol	parts by weight	10	20	40	—	—	36	32
2,6-Dihydroxymethyl- <i>o</i> -cresol	parts by weight	—	—	—	40	40	4	8
Vulcanization temperature	° C	155	155	155	200	200	155	155
Tensile strength	kg. per sq. cm.	22	100	170	36	85	70	42
Elongation at break	percentage	575	575	558	450	490	460	450
Modulus at 100%	kg. per sq. cm.	3	6	6	*	5	5	3
Modulus at 200%	kg. per sq. cm.	5	10	15	*	8	10	6
Modulus at 400%	kg. per sq. cm.	8	29	83	*	50	48	29
Hardness	Shore A.	30	35	38	*	30	30	25

\* Not determined.

To this end diphenol, bis(2-hydroxy-3-methylphenyl)methane (XIV), was synthesized as a starting material<sup>10</sup>. The dihydroxyphenol (XV) could not be successfully prepared from this diphenol but the substance was obtained in a somewhat impure state.

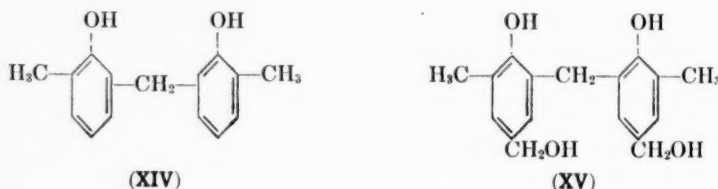


FIG. 5.

This preparation was carried out as follows:

A mixture of 11.4 grams of bis(2-hydroxy-3-methylphenyl)-methane (XIV), 80 grams of a 10 per cent solution of sodium hydroxide and 36.4 grams of a 33 per cent aqueous solution of formaldehyde was kept at a temperature of 10–11° C for seven days. The solution was then diluted with 750 cc. of water and acidified continuously with a mixture of 75 cc. of 4 *N* acetic acid and 750 cc. of water. The voluminous precipitate of compound XV was filtered off, washed thoroughly with water, and dried. The final product was composed of white crystals, melting at 178–182° C (with decomposition). The yield was 14 grams or 97 per cent.

A small part was recrystallized from a mixture of ethyl acetate and petroleum ether (b.p. 40–60° C); the substance is difficultly soluble in the latter. The highest melting point which could be obtained was 222.5° C (with decomposition). The purification could not be continued for lack of solvents, particularly petroleum ether. Analysis:

Substance: 41.6 mg.; CO<sub>2</sub> 106.4 mg.; H<sub>2</sub>O 25.3 mg.

Found: C 69.75; H 6.77

Calculated for C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>: C 70.82; H 6.95

It was thus possible to isolate a crystallized compound, the C–H analysis of which corresponded fairly well with the calculated values. However, the

compound was more or less impure because of the unfavorable conditions. Accordingly the vulcanization tests had to be carried out with a relatively impure compound. The following results were obtained.

A mixture of 100 parts of rubber and 40 parts of the impure dihydroxyphenol (XV) showed, when heated in nitrogen for 2 hours at 155° C almost no vulcanization; 2 hours at 200° C brought about some vulcanization, and after 2 hours at 220° C a quite obvious vulcanization reaction was observed. However, even in the latter case the product was still sticky, though entirely insoluble in benzene.

That these vulcanizations did not give better results should undoubtedly be attributed to the unfavorable influence of the impurities. Repeated washing of the dihydroxyphenol (XV) with ethyl acetate, in which the compound, unlike the starting phenol (XIV), is difficultly soluble, increased slightly the vulcanizing power. However, in these cases too sticky products were obtained, the mechanical properties of which could not be determined.

Although no better results could be obtained because of the unfavorable conditions, it may at least be concluded from the above that the bis-hydroxyphenol XV has vulcanizing properties. Since this compound cannot react with a rubber molecule to form a chromane derivative, because of the *para*-position of its alcohol groups, vulcanization in this case certainly must be formulated in some other way. According to the "methylene quinone theory", a short survey of which is given at the end of this article, this vulcanization involves the formation of a double *p*-methylenequinone (XVI) as an intermediate.

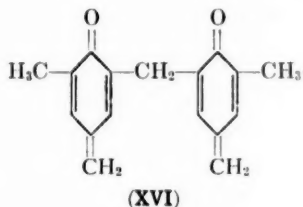


FIG. 6.

As was found by the vulcanization experiments with 2,6-dihydroxymethyl-*o*-cresol, the formation of a *p*-methylenequinone requires the relatively high temperature of about 200° C. This gives strong support to the concept that vulcanization with this compound takes place through the formation of *p*-methylenequinones. Accordingly also the vulcanization temperature of the bis-hydroxyphenol, XV, is high, *viz.*, 200–220° C.

#### Conclusion. Methylenequinone theory.

From what has been described above, it may be concluded that the chromane theory is inadequate to explain the vulcanization mechanism of phenol-formaldehyde derivatives. On the other hand, it appears possible to explain all the phenomena observed by means of the methylenequinone theory. The essential part of this theory, which has been described in detail in the author's thesis, can be formulated in brief as follows:

The vulcanization reactions of phenol-formaldehyde derivatives are based on the formation of methylenequinones as intermediate compounds

under the influence of high temperatures. A methylenequinone formed in this way combines, at least in part, spontaneously with a rubber molecule to form an addition compound, the original phenol structure being reformed at the same time. This initial addition compound is reconverted into a compound with a methylenequinone structure under the influence of the high temperature. The latter combines spontaneously with another molecule of rubber to form a vulcanizate. So in this case too vulcanization must be explained by the formation of bridge linkages between the rubber molecules.

The vulcanization process according to the above theory is given in Figure 7 with 2,6-dihydroxymethyl-*p*-cresol as an example.

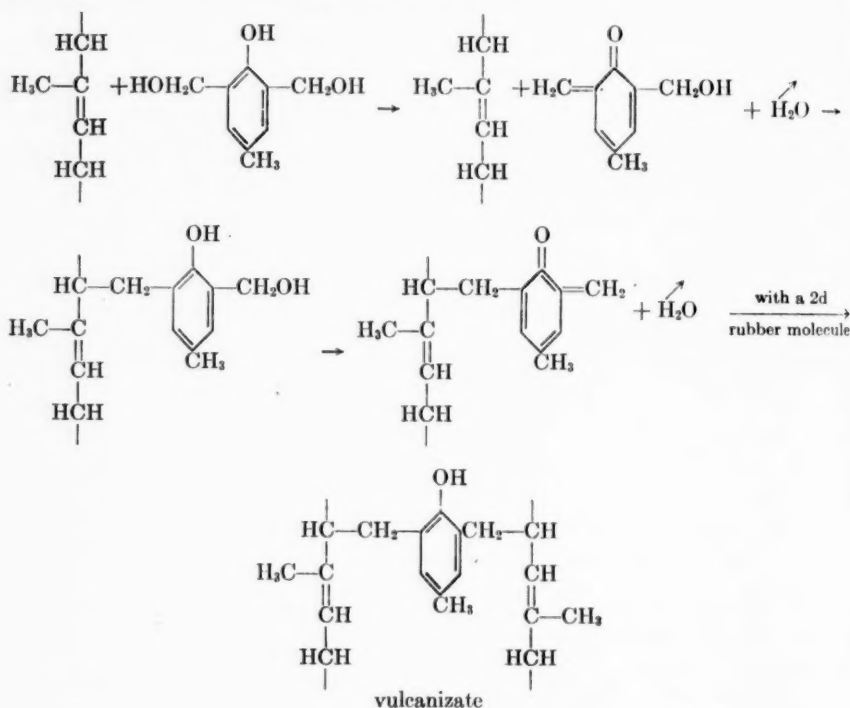


FIG. 7.

The results of the investigations, carried out to test this methylenequinone theory, can be summarized as follows.

1. The vulcanizing properties of pseudo-phenol halides are based on the ready transformation of these compounds into methylenequinones, with liberation of gaseous hydrogen halide.
2. The vulcanizing properties of dihydroxyphenols depend also on the formation of methylenequinones as intermediate compounds, this reaction occurring, however, at a higher temperature.
3. Dihydroxyphenols vulcanize slowly at temperatures only a little below their decomposition temperatures, and yield comparatively good vulcanizates.

Pseudo-phenol halides vulcanize rapidly at temperatures considerably below their decomposition temperatures, and yield comparatively poor vulcanizates.

4. The vulcanization temperature of 2,6-dihydroxymethyl-*o*-cresol (about 200° C) is higher than that of 2,6-dihydroxymethyl-*p*-cresol (about 155° C), as in the first case the vulcanization is based on the formation of both an *o*- and a *p*-methylenequinones. These latter compounds are generally formed more easily than are the *p*-isomers.

5. The vulcanizing power 2,6-dihydroxymethyl-*p*-cresol at 155° C is reduced by the addition of 2,6-dihydroxymethyl-*o*-cresol, in consequence of the formation of such molecule complexes, which are unable to form *o*-, but only *p*-methylenequinones.

6. The vulcanizing power of phenol-formaldehyde derivatives is entirely nullified by hexamethylenetetramine, since this compound combines with the methylenequinones first formed.

7. The vulcanization reactions of the phenol-formaldehyde derivatives do not depend on the formation of irregular knots of entangled rubber and resin molecules, but on primary chemical bonds between these two.

8. The vulcanizing properties of esters of dihydroxyphenols are based, like those of pseudo-phenol halides, on the formation of methylenequinones as intermediate products, with liberation of acids. The higher fat acid esters of 2,6-dihydroxymethyl-*p*-cresol are unstable, and liberate acids even at room temperature.

9. Compounds that may be supposed to be derived from dihydroxyphenols by changing the structure of the latter do not show vulcanizing properties if a repeated methylenequinone formation is excluded. Since in the case of hydroxyphenols this is possible only to a very limited extent, the vulcanizing properties are present to only a minor degree.

It is clear that these results not only confirm the methylenequinone theory, but at the same time preclude the chromane theory as an explanation of the mechanism of vulcanization of phenol-formaldehyde derivatives.

#### ACKNOWLEDGMENT

The author wishes to express his gratitude to A. Van Rossem, Director of the Research Department of the Rubber Foundation, for his great interest in these investigations.

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## VULCANIZATION OF GR-S BY THE PEACHEY PROCESS \*

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It has been found possible to vulcanize GR-S synthetic rubber by subjecting it alternately to hydrogen sulfide and sulfur dioxide gases. This method for curing, known as the Peachey process<sup>1</sup>, was used for natural rubber as long ago as 1921.

A simple apparatus was constructed, in which strips of thinly milled rubber were placed on a screen inside a glass tube. One end of this tube was attached to valves connecting it to tanks of hydrogen sulfide, sulfur dioxide, and air, respectively. The other end of the tube led to a series of traps containing solutions which absorbed or destroyed the gases.

For each test performed, natural rubber samples were placed inside the tube along with the GR-S samples for comparison. Each strip was weighed before it was inserted in the apparatus. Hydrogen sulfide was first slowly passed over the samples for a period of five minutes. Then air was blown through for a few seconds—just long enough to free the surroundings from the sulfide gas, but not long enough for the gas to be lost from solution in the rubber. Sulfur dioxide gas was next admitted and allowed to pass over the samples for five minutes. A subsequent short sweep of air through the tube completed one cycle of the curing process.

Tests were made on both the natural rubber and the GR-S samples from one cycle of operation to twenty-four cycles. After the samples had been removed from the apparatus and allowed to stand until equilibrium weight had been established at room conditions, they were weighed. The increase in weight was assumed to be chiefly sulfur, both in the free and the combined forms. Hand-stretching was performed on the samples to determine the state of cure. The results can be summarized in the accompanying table.

No. of cycles	Natural rubber		GR-S	
	Increase in weight (%)	State of cure	Increase in weight (%)	State of cure
1	1.2	Slight undercure	0.2	None
2	3.5	Optimum cure	0.4	None
3	6.6	Slight overcure	0.8	Noticeable
4	7.0	Slight overcure	1.0	Noticeable
6	10.0	Considerable overcure	2.4	Slight undercure
12	11.8	Leatherlike	4.2	Optimum cure
24	13.0	Leatherlike	9.7	Slight overcure

\* Reprinted from *The Rubber Age* (New York), Vol. 59, No. 3, page 323, June 1946.

It can be seen from the table that the GR-S vulcanizes much more slowly than the natural rubber by the Peachey Process. However, it was possible to get an optimum cure and even an overcure with the GR-S by this process.

#### ACKNOWLEDGMENT

At my suggestion, my associates, Norman Bekkedahl and Fred A. Quinn made the simple exploratory experiments described in this note. They are proceeding with a more thorough study.

#### REFERENCE

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## PLASTICIZERS IN RUBBERS AND PLASTICS \*

H. JONES

Up to the advent of synthetic high polymers, plasticizer technology was little understood. Plasticizers had been used mainly with cellulose derivatives, which are not at all good materials for the study of plasticizer action. The chemical processing they undergo, *e.g.*, nitration, acetylation, etc., leads to variations on account of irregular chemical action. In addition, these materials are partly crystalline and partly amorphous. The growing numbers of new materials brought a host of problems in their train, and plasticizing was not the least of them, but a study of their behavior with plasticizers has advanced the knowledge of the plasticizer-polymer system.

The principal advances have come from a study of regular and amorphous polymers, such as polyvinyl chloride, polyvinyl acetate, polystyrene, butadiene rubbers, and so on. From knowledge of these materials, one can revert to the consideration of irregular polymers such as cellulose derivatives and those produced from high polymers by additional chemical reaction, with a better likelihood of understanding their behavior with plasticizers.

Thus the recent extensive use of plasticizers has led to an improved understanding of their action, and it appeared that a paper dealing with the subject might be acceptable.

**THE FUNCTION OF PLASTICIZERS.**—Plasticizers are stable chemical compounds of low volatility, capable of permanent miscibility with polymers. They function by separating the chains which comprise the polymer structure and so reduce the magnitude of the intermolecular forces. Consequently they render the mass more mobile and extensible.

They are best regarded as complementary materials to cross-linking or vulcanizing agents. This is an approach to the subject that becomes evident by considering the effects of the two types of materials with respect to such properties as hardness, tensile strength, softening point, flexibility, cold flow, and so on.

In many cases plasticizers produce undesirable effects, whereas in others their use is vital. For example, with high polymers, such as cellulose acetate and polyvinyl chloride, whose softening points are uncomfortably near their decomposition points, the use of plasticizers is essential in order that moulding or other shaping processes may occur.

Figure 1 gives a picture of the polymer-plasticizer system, polyvinyl chloride and dibutyl phthalate being selected for illustration. The basis of a polymethylene chain is taken, and variations due to the single and conjoint use of plasticizer and cross-linking agent are shown. This is approximately to scale, though the distension of the chains in the case of simple plasticizer addition is doubtless much greater than shown.

At first sight it might be thought that the ideal method of controlling the properties of a polymer would be by the correct choice of monomer and its

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 5, pages 298-321, February 1946.

polymerization, especially by the control of its degree of polymerization and the molecular-weight distribution. This is true but not always practicable. Furthermore it would call for the production of a specific polymer for each use. This is not feasible at the present time and probably never will be.

The selective variation of the properties of a polymer by the appropriate use of plasticizers enables a much wider range of properties to be obtained. One can choose a polymer most suited for a given purpose and modify it at will, in much the same way as the rubber technologist varies the compounding and curing of each type of rubber in which he is interested.

Two variations on the theme of polymer modification seem worth mentioning at this stage.

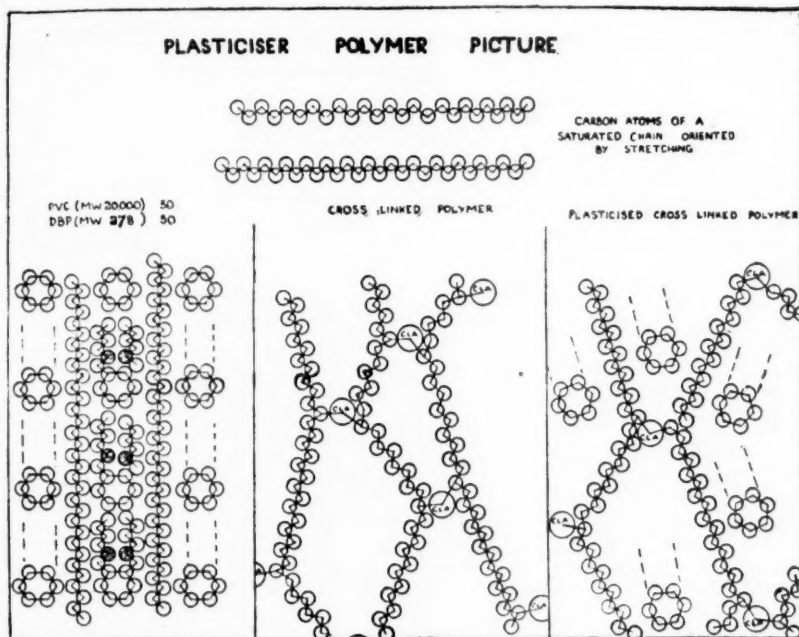


FIG. 1.

*Self-plasticizing polymers.*—There are numerous polymers which are described as self-plasticizing. In other words the nature and number of the side groups on the main polymer chain is such as to bring about an appreciable chain separation and so give properties akin to those produced by the use of plasticizers. Homologous series based on the polyacrylates and methacrylates, cellulose derivatives such as ethyl cellulose and cellulose acetate-butyrate are of this type, but even here the properties rarely meet all requirements, and the use of discrete amounts of plasticizers is standard practice.

*Vulcanizing plasticizers.*—These would appear to have the object of coupling the two properties suggested by their name in the sense that, since they are compounds of large molecular size, they produce chain separation and yet, since they are reactive either to the polymer or themselves, they fix or cross-link the chains. The result is a more extensible and softer product having an

increased softening point and tensile strength. Their use is similar to the process of plasticizing and cross-linking certain of the synthetic rubbers such as Hycar-OR by the conjoint use of sulfur and plasticizers.

It is necessary to consider three further aspects, the first of which is the choice of a plasticizer for a given polymer, the second its retentivity. The final point to be dealt with is the resultant properties of the masses arising from these combinations, and here it is hoped to illustrate the close connection between the physical properties of the plasticizer and those of the compounds made by its use.

**MISCIBILITY OF PLASTICIZERS AND LIQUIDS.**—Recent ideas on the swelling and dispersion of polymers in liquids are based on the recognition of polymers as liquids. Solvent action then becomes a process of liquid-liquid mixing which, in turn, is the reason for the use of the word miscibility of plasticizers and polymers in place of compatibility<sup>1</sup>.

TABLE 1  
QUALITATIVE MISCIBILITY TESTS OF PLASTICIZERS AND POLYMERS

	C.A.	E.C.	P.V.C.	P.V.B.	B.S.	B.A.N.
Dimethyl phthalate	gg	g-gg	gs	gs	gn-gs	gg
Diethyl phthalate	gs	g-gg	gs	gs	gn-gs	gg
Dibutyl phthalate	gs	g	g-gg	gs	gn-gs	g
Diamyl phthalate	gn	—	g	gs	gs	g
Dihexyl phthalate	gn	—	g	gn-gs	gg	gs
Diocetyl phthalate	gn	gn	g	gn-gs	gs-g	gn-gs
Dicetyl phthalate	gn	gn	gn	gn	—	—
Dimethylglycol phthalate	gs	gn-gs	gn-gs	—	gn	gs
Diethylglycol phthalate	gs	gs	gn-gs	gs	gn	gs
Dibutylglycol phthalate	gn	g-gg	gg	—	gn-gs	gs
Trimethyl phosphate	gg	gn	gn	gs	—	—
Triethyl phosphate	gg	gs-g	gs	gg	—	—
Tributyl phosphate	gn	g-gg	gg	gg	gn-gs	gg
Tricresyl phosphate	gn	gs-g	gg	gs	gn-gs	gs
Trichloroethyl phosphate	gg	gs	gn	gn	gn	gs
Trimethylglycol phosphate	gg	gn-gs	gn-gs	gs	gn	gs
Triethylglycol phosphate	gs	—	gs	—	gn	gs
Tributylglycol phosphate	gn	g	g	—	gn-gs	gs

Polymers:—C.A. (cellulose acetate); E.C. (ethyl cellulose); P.V.C. (polyvinyl chloride); P.V.B. (polyvinyl acetate-butylal); B.S. (butadiene-styrene); B.A.N. (butadiene-acrylonitrile).

The oft-discussed question of why and how a plasticizer attaches itself to a polymer becomes more easily understood on these lines, and the system lends itself to ordinary thermodynamical treatment. Space does not allow a discussion of this part of the subject, but probably all the phenomena met in text-book considerations of binary systems, etc., are encountered in plasticizer technology, though they may not always be immediately recognized. Most types of secondary bonds are at play in these mixing processes, the so-called van der Waals forces, hydrogen bonds, polar forces, etc., and likewise the several types of mixing, ranging from surface action, such as capillary imbibition to intermicellar swelling. In the case of partly crystalline polymers such as cellulose acetate, and probably in other oriented polymers, both inter- and intramicellar swelling and dispersion can occur according to the particular solvent or plasticizer in use.

For practical purposes several methods of determining the miscibility level are available. One can simply mix small amounts of polymer and plasticizer and observe the swelling or dispersion that occurs either at room temperature or

above. The main stages of mixing can be classified as follows, and the term "gelling" is employed to describe the results in Table 1.

gg, good gelling, when swelling and dispersion to a clear homogeneous solution take place in a matter of a few hours. This constitutes unlimited miscibility.

g, gelling of an inferior type, characterized by a cloudiness of the solution and a certain lack of homogeneity owing to the presence of the original grain structure of the polymer. Even in this case the miscibility of the plasticizer with the polymer may be several hundred per cent.

gs, slight gelling or swelling of a limited nature, with definite evidence of two phases which appear to comprise liquid plasticizer and swollen grains of polymer. In this case the miscibility may be of the order of 50-100 per cent.

gn, no gelling. The polymer may be wet out and small amounts of plasticizer may actually have mixed with the polymer, *e.g.*, up to about 50 per cent by weight.

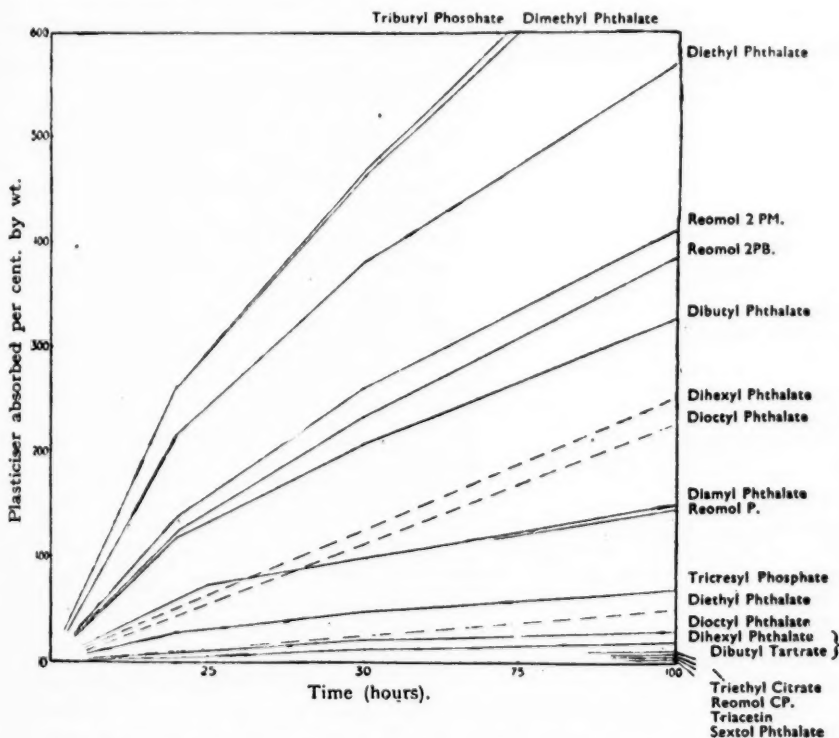


Fig. 2.—Swelling of synthetic rubbers in plasticizers. Hycar OR-15 — Hycar TT- - -

Table 1 shows the results of a typical series of simple tests of this nature. More exact methods of the determination of the miscibility depend on the actual preparation of a series of compounds varying by 5 per cent amounts. The aging of these materials enables the numerical value for the mixing to be

obtained to a closer degree, but the only true method is to immerse polymers in plasticizers and record the increase in weight by means of a swelling curve.

Figure 2 shows the swelling of Hycar-OR and -TT in a series of plasticizers. The case of unlimited mixing may be recognized easily, and the intermediate stages can all be assigned numerical values. With limited swelling, little or no polymer passed into the plasticizer in this test.

By these methods one can arrive at a safe figure for the use of a given plasticizer for a given polymer, though in the case of cross-linked polymers it is advisable to determine the effect after curing, that is to measure the miscibility with an unplasticized but vulcanized specimen of material (Figure 3).

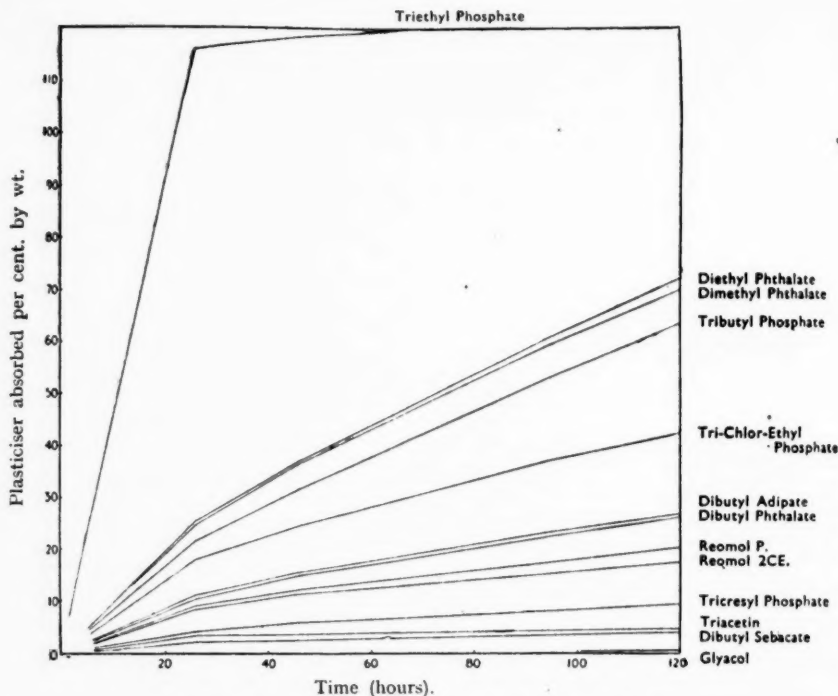


FIG. 3.—Swelling of Vulcanized Hycar OR-15 in Plasticizer.

Figure 4 shows a hypothetical diagram of state of polymer and plasticizer, this again being on the liquid-liquid basis of mixing. Curve 1 shows a case of complete miscibility at temperatures above  $0^{\circ}\text{C}$ . This would correspond to good gelling. Curve 2 shows a pair which are miscible in all proportions only at temperatures above  $100^{\circ}\text{C}$ ; cooling of the solution in this case would lead to a two-phase system, still technically useful. Curve 3 shows a pair of substances which are only miscible in all proportions over  $174^{\circ}\text{C}$ . Here mixing or gelling takes place at high temperatures, but cooling leads to the same change of state as with curve 2, except that the two phases are different. This corresponds to limited miscibility and is technically undesirable, as the plasticizer will exude or sweat out from the compound on standing. For complete miscibility over the wide range of temperatures experienced in service conditions

today, behavior of the type of curve 1 is desirable, unless of course the ratio of plasticizer and polymer is still in the miscible areas of the other examples. Some plasticizers in common use today are of the type pictured in curve 3, examples being butylacetyl ricinoleate and chlorinated paraffin wax in polyvinyl chloride. In many of these cases the separation of plasticizer or the reversion to two-phase systems is not always immediate. Probably the supercooling effect due to the high viscosity of the system prevents this happening quickly, but use of the compound at temperatures much above room temperature would accelerate the separation with possibly disastrous results. The question of the use of more than one plasticizer complicates the subject, but

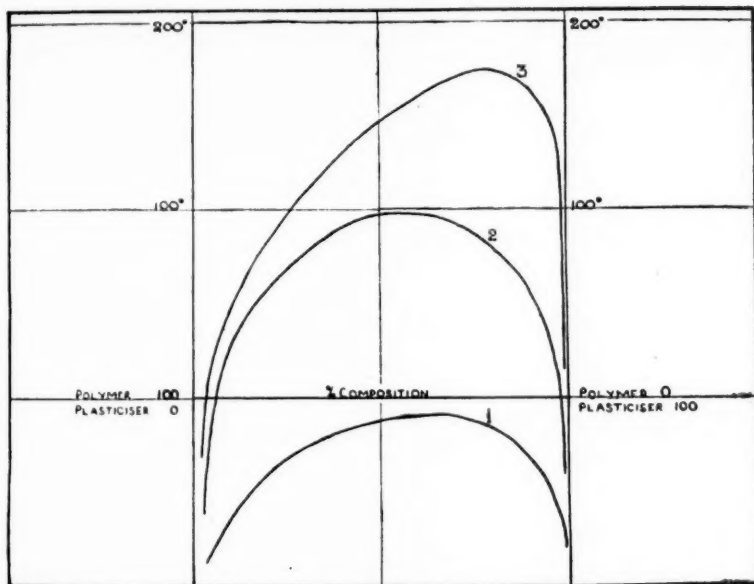


FIG. 4.—Hypothetical diagrams of state of polymer-plasticizer systems.

1. Polymer and plasticizer miscible in all proportions at 0° C. Mixing proceeds.
2. Miscible in all proportions only >100° C. Cooling of solution ultimately gives 2 phases—both technically useful.
3. Miscible only above 174° C. Cooling gives 2 phases—one consisting of almost 100 per cent plasticizer technically undesirable.

it seems that an extension of Gee's work<sup>2</sup> on the behavior of rubber and solvents, as suggested by Tuckett<sup>3</sup> might be useful if the necessary physical data on the cohesion energy densities of plasticizers could be obtained. This would apply equally to the mixing of a single plasticizer.

**RETENTION OF PLASTICIZERS.**—This is a necessary part of the technology of plasticizer working, and really constitutes the aging of plasticized compositions. Aging can occur with respect to the plasticizer, by loss in air (which is evaporation) or by the leaching action of liquids.

**Loss by evaporation.**—The loss in this case is controlled in the first instance by the vapor pressure of the plasticizer and its rate of diffusion through the polymer-plasticizer mass. Usually the boiling point at either room temperature or under reduced pressure is taken as an index of the rate at which a plasticizer evaporates and for many practical purposes in dealing with a homologous



series of materials this is useful. Since it is difficult to measure the vapor pressure at room temperature it is more usual to measure the weight loss with time at slightly higher temperatures, *e.g.*, 100° C. This has a more practical significance, as plastics and rubbers are frequently required to serve at high temperatures, and measurable rates of evaporation are possible.

Figure 5 shows a number of plasticizers and their rate of evaporation in the free state in relatively static air. By the data obtained from this type of work one can usually segregate plasticizers into those likely to give good or indiffer-

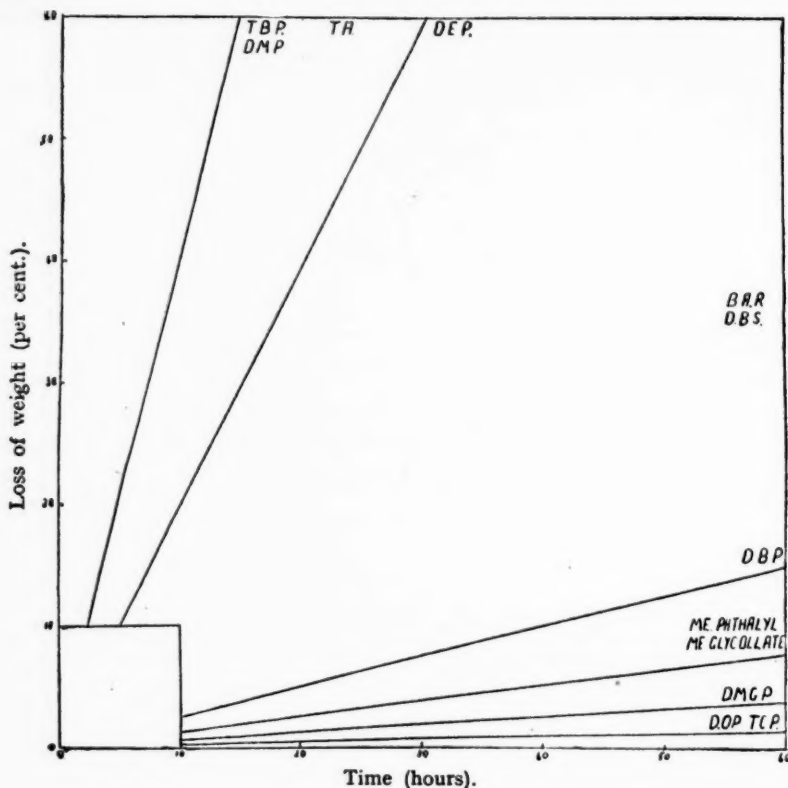


FIG. 5.—Volatility of plasticizers.

ent aging. Plasticizers with boiling points above 400° C are most desirable; this generally corresponds to weight losses in static air at 100° C of about 5 per cent after 100 hours.

The most reliable method is to age the plasticizer-polymer mixture at elevated temperatures to incorporate any effect of the plasticizer-polymer interaction. One needs only to recall the good aging properties of the nitrocellulose camphor complex to realize that there are limitations to the evaluation of plasticizer evaporation by tests in the free state. Recent work on the aging of plastics is likely to be of interest to rubber technologists, especially since they are now using plasticizers of different kinds in synthetic rubbers. Previously, the aging of plasticized materials has been carried out at elevated tem-

peratures in relatively still air. Nowadays, ideas demand that a high rate of air displacement should be used, as still air can soon become saturated with plasticizer vapor and thus restrict further losses<sup>4</sup>.

Table 2 shows some collected aging tests on polyvinyl chloride compounds made with various plasticizers. The results are shown for two methods, one being the so-called standard aging of the type used in the rubber trade, the other the accelerated aging method involving an air displacement of several cubic feet per minute through the test oven.

Table 3 gives aging results on a series of Hycar OR-15 compounds covering several different types of plasticizers. The change of tensile strength on aging is clearly evident, as is also the connection with the actual weight loss of the

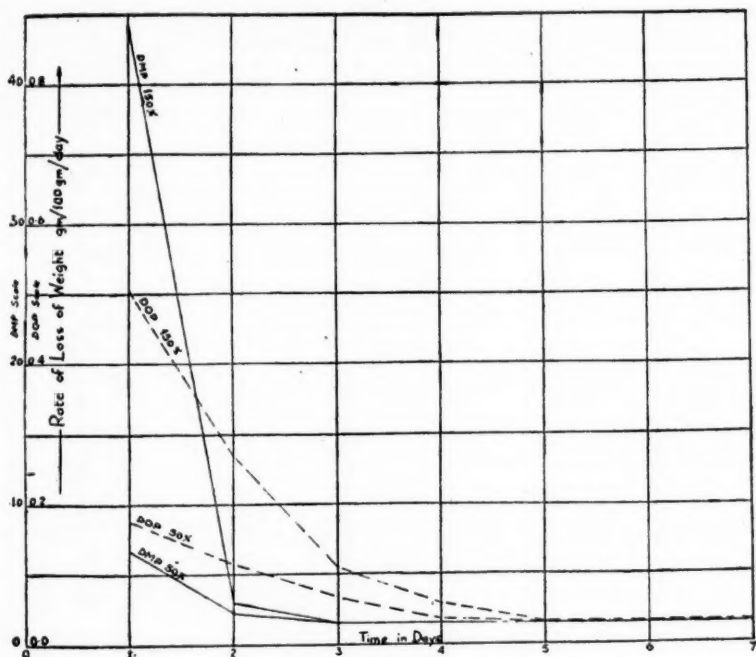


FIG. 6.—Aging of plasticized PVC. — DMP - - - DOP.

test-specimens. Both types of aging are present here, oxygen aging of the rubber and plasticizer aging by evaporation. These effects oppose each other, and in the case of dimethylglycol phthalate are approximately equal, there being no loss of tensile properties. The elongation at break decreases in all cases; no connection with percentage weight loss appears in this case. The first effect in aging is a rapid one due to surface evaporation of the plasticizer, but later, as the surface becomes denuded, the slower diffusion rate predominates.

Figure 6 gives some idea of the relative rates of these processes and of the effect of high and low plasticizer concentration with two plasticizers, dimethyl and dioctyl phthalates in polyvinyl chloride. Not much is known of the diffusion rates, although attempts have been made to determine them. The most one can say at present is that they are extremely slow, the size of the molecule



TABLE 3  
PHYSICAL PROPERTIES OF PLASTICIZED COMPOUNDS BASED ON HYCAR OR-15

No.	Plasticizer (in order of viscosity)	$\eta$ at 20° cts.	T <sub>b</sub> (lb. per sq. in.)		Per cent gain		Ex (per cent)			BSS hard-ness	Low temp. flex limit 25 g. per sq. mm. °C	Weight loss (per cent) 75° C accelerated
			Unaged	Aged	Unaged	Aged	Unaged	Aged	Per cent gain			
1.	None	—	3209	2571	—20	—20	328	285	—13	30	—15	1.2
2.	Reomol-2CE	281	3055	3244	+6	—	444	350	—20	47	—21	1.4
3.	Tricresyl phosphate	80.9	3033	2642	—12	—10	575	516	—10	53	—25	1.6
4.	Dioctyl phthalate	79.4	2767	2376	—14	—9	546	496	—9	64	—36	2.8
5.	Dimethylglycolphthalate	41.6	2729	2877	+5	0	500	502	0	57	—36	6.5
6.	Trichloroethyl phosphate	30.2	2790	3877	+36	—18	550	498	—18	56	—37	11.8
7.	Dibutyl phthalate	19.8	2567	3324	+29	—10	590	523	—10	61	—42	16.9
8.	Dibutyl sebacate	9.6	2421	—	—	—	580	—	—	70	—44	9.0
9.	Tributyl phosphate	3.98	1630	2860	+43	—31	511	350	—31	65	—51	19.0
	Hycar OR-15	100	parts by weight						Sulfur	1.5	parts by weight	
	Zinc oxide	5	parts by weight						China clay	50	parts by weight	
	Dibenzothiazyl disulfide	1.5	parts by weight						Stearic acid	0.5	parts by weight	
	Phenyl- $\beta$ -naphthylamine	1.5	parts by weight						Plasticizer	40	parts by weight	

is very important and that the usual diffusion factors of time, temperature and concentration gradient apply. No reliable conclusions seem to be available as to the actual diffusion constant for any particular system, as the results of Liebhafsky, Marshall and Verhoek<sup>5</sup> are not confirmed by Reed<sup>4</sup> and are disputed by the practical experience of the author.

*Loss by solvent action.*—Four processes can occur when a plasticized compound is immersed in a liquid, (1) liquid absorbed by polymer; (2) liquid absorbed by plasticizer; (3) polymer passed into liquid; and (4) plasticizer passed into liquid. Only those concerning the plasticizer are of interest in this paper.

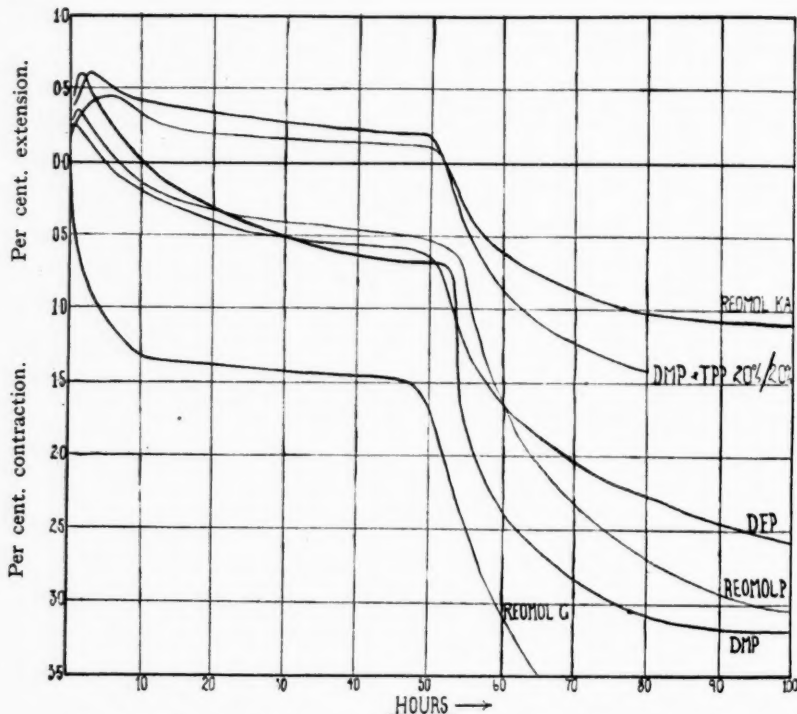


FIG. 7.—Water immersion curves for cellulose acetate plus 40 per cent plasticizer.

The behavior of a plasticized compound in a liquid can best be regarded as the distribution of the plasticizer between the polymer and the liquid, and for this the most useful data are of course the miscibilities of the plasticizer with these two components. Some ideas on mixing polymer and plasticizer have been given, and measurements of the solubility of plasticizer in water or other liquids and *vice versa* are easily made.

For good aging in contact with water, plasticizers should have a solubility of less than 0.01 per cent at room temperature and but little more at elevated temperatures. Many plasticizers in current use have water solubilities of 0.1 per cent; these can hardly be expected to age well in contact with water.

Figure 7 shows the effect of water immersion on plasticized cellulose acetate. This is a special type of test used by the film industry<sup>6</sup>, but it is clear that there

is a close relationship between the water solubility of the plasticizer and its retention in a polymer. The first process consists in the absorption of water, but later the loss of plasticizer becomes equal to this and an equilibrium condition is reached. Drying-out of the water at a later stage of the test reveals the extent to which the plasticizer has been removed.

Figure 8 shows the mixing of plasticizers with gasoline as an indication of their likely behavior in rubber compounds.

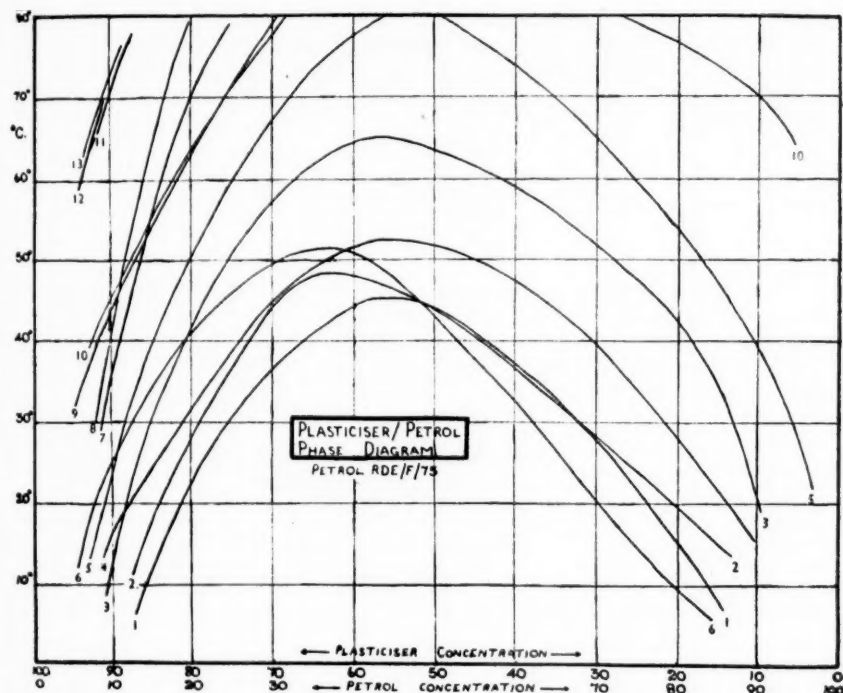


FIG. 8.

- |                                   |                                 |
|-----------------------------------|---------------------------------|
| 1. D.M.P.                         | 8. Di(ethyl carbitol) phthalate |
| 2. Methylphthalylethyl glycollate | 9. Polyglyceryl ester           |
| 3. D.M.G.P.                       | 10. Glycerollactate diacetate   |
| 4. ethylphthalylethyl glycollate  | 11. Diglyceryltetracetate       |
| 5. Reomol-2CE                     | 12. Diacetin                    |
| 6. Phenylglycol ether             | 13. Triacetin                   |
| 7. Di(methyl carbitol) phthalate  |                                 |

The following plasticizers are completely miscible at 20° C.

Diethyl phthalate	Di(ethoxyethyl) phthalate	Dibutyl malonate
Diisopropyl phthalate	Di(butoxyethyl) phthalate	Dibutyl succinate
Dibutyl phthalate	Reomol-BCP.	Dibutyl adipate
Diamyl phthalate	Butylphthalylbutyl glycollate	Dibutyl sebacate
Dihexyl phthalate	Tributyl phosphate	Butylacetyl ricinoleate
Diethyl phthalate	Tricresyl phosphate	Methoxyethylacetyl ricinoleate
Diethyl phthalate	Dibutyl oxalate	

Figure 9 shows the effect of gasoline and oil on plasticized Hycar OR-15 compounds. Here again the relation of the solubility of the plasticizer in gasoline is shown in the maximum swelling and leaching with plasticizers of highest solubility in gasoline. These curves have some interesting aspects. Gasoline enters the polymer mass as water enters cellulose acetate. Later the



loss of plasticizer increases until it becomes the predominating effect. In the case of oil immersion, the immediate loss of plasticizer is the main feature of each curve. This may be due to the higher viscosity of the oil. The initial rates of absorption of gasoline appear to be related to the viscosity of the plasticizer, although dioctyl phthalate (DOP) shows an irregular behavior.

**PROPERTIES OF THE PLASTICIZER—POLYMER SYSTEM.**—With certain limitations it is possible to predict the physical and other properties of a compound when the physical properties of the polymer and plasticizer and the ratio of their use is known.

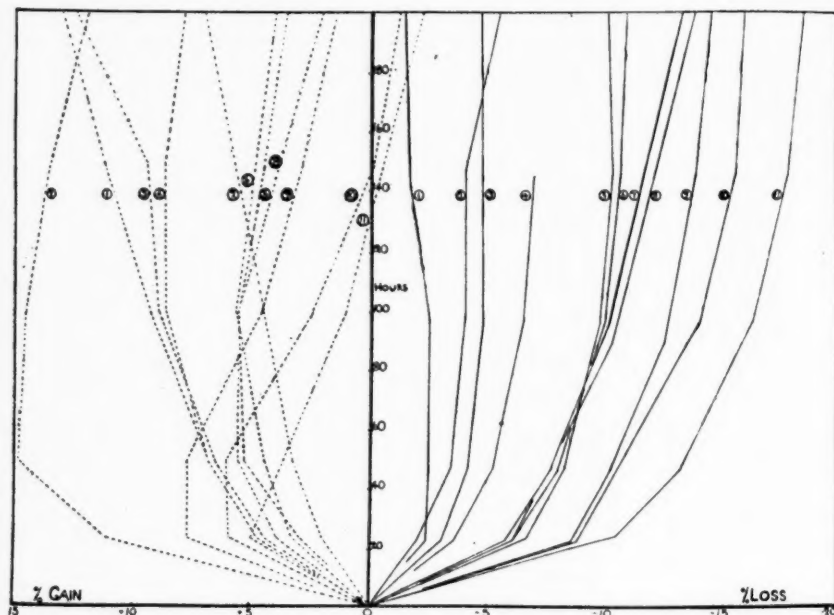


FIG. 9.—Effect of oil and gasoline on Hycar OR-15 compounds.

Oil DTD44D — Gasoline RDE/F/75 - - - -				
1 None	3 TCEP	5 DMGP	7 DOP	9 TBP
2 DCEP	4 Plassitil	6 TPP	8 TCP	10 DBP
				11 DBS

Figure 10 shows a hypothetical mixing diagram of a polymer and a plasticizer on the viscosity basis. This is legitimate if one continues to regard the mixing as the mixing of two liquids. The scale used is log-log kinematic viscosity against percentage composition. This is a well known method of determining the viscosity properties of similar liquids and similar polymers in solution. For similar liquids it is used in the petroleum industry, and in the cellulose industry it is used to determine the solution viscosities of mixtures of ethyl- and nitrocelluloses of different viscosities and also for mixtures of different cellulose derivatives.

The viscosity of the polymer is extremely high at room temperature (several millions of centistokes), whereas that of the plasticizer is usually below 500 centistokes. In fact most commercial plasticizers are less than 100 at room temperature.

From this picture one can appreciate two main points: first, the outstanding effect of the percentage of plasticizer in the composition, and, second, the smaller, but significant effect of the viscosity of the plasticizer used.

The limitations to this concept of the properties of mixtures are first, that complete mixing or solution should occur, and second, that no irregularities such as association or compound formation take place. The limitations are most likely to be shown in the case of irregular polymers such as cellulose derivatives where the mixing with plasticizers may only be partial, *i.e.*, the crystallites are unaffected. The picture is reminiscent of the usual diagram of state of two liquids, and this immediately brings to mind some of the probable deviations from linearity of the curves shown. This is not unlikely, as mentioned, but it is doubtful whether significant variations occur or whether the curves deviate substantially from being linear. This is particularly the case

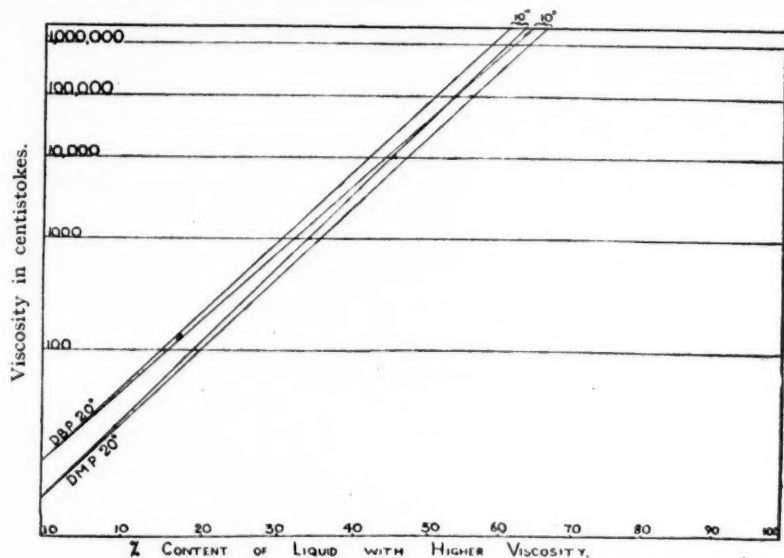


FIG. 10.—Viscosity of plasticized polymers.

on account of the extreme difference between the properties of the polymer and the plasticizer, and on account of the scale used.

The two examples (Figure 10) relate to a fixed temperature, and as the variation of viscosity of liquids with temperature is linear on the log-log scale, the effect of temperature is simply to move the lines upwards or downwards in a parallel fashion. The displacement ceases to be parallel if the slope of the viscosity temperature curve of the plasticizer is different from that of the polymer, and *vice versa*. Although this is a hypothetical set of curves, and indeed little is yet known of the viscosity of polymers in their pure state, and furthermore their behavior at room temperature is confused by concepts that part of their flow phenomena are not wholly viscous, one can proceed with more confidence to the part of them which comprises the main subject, namely, the plasticizers.

The study of the viscosity of plasticizers and its variation with temperature dates back some two or three years, and a few comments on the origin of the

subject may be of interest. Before 1939 little attention had been paid to the effect of low temperatures on the performance of rubbers and plastics, though the need to do so had been well realized. Demands arising from their use at subzero temperatures and the introduction of new materials which, unlike natural rubber, had not quite the same sustained behavior over wide temperature changes, called for more knowledge in these respects. It had been realized

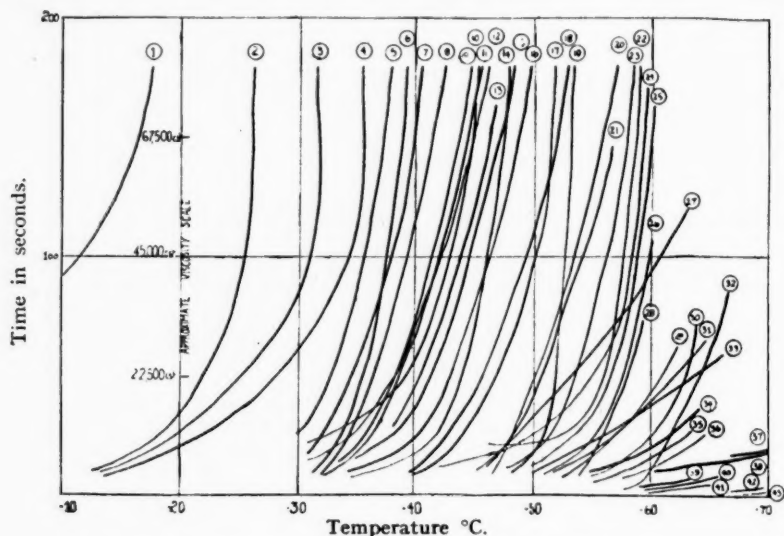


Fig. 11.—Low temperature viscosity of plasticizers.

- |                                  |                             |
|----------------------------------|-----------------------------|
| 1. Glycerol lactate-acetate      | 23. Reomol-P2MG             |
| 2. Tricresyl phosphate           | 24. DTD44/D oil             |
| 3. Ethylphthalylethyl glycolate  | 25. Butylacetyl ricinoleate |
| 4. Reomol-P                      | 26. Reomol-2PE              |
| 5. Reomol-2CM                    | 27. Reomol-NF2              |
| 6. Polyglyceryl ester            | 28. Reomol-12J              |
| 7. Triamyl citrate               | 29. Dibutyl phthalate       |
| 8. Triethyl citrate              | 30. Reomol-2MC              |
| 9. Dihexyl phthalate             | 31. Reomol-2PB              |
| 10. Reomol-2CE                   | 32. Triglycol dioctoate     |
| 11. Butylphthalylbutyl glycolate | 33. Reomol-3EJ              |
| 12. Dioctyl phthalate            | 34. Reomol-G acetate        |
| 13. Triacetin                    | 35. Reomol-2BC              |
| 14. Reomol-2CB                   | 36. Reomol-PEEX             |
| 15. Reomol-2B                    | 37. Reomol-2EC              |
| 16. Diamyl phthalate             | 38. Reomol-3BJ              |
| 17. Reomol-GO                    | 39. Reomol-3MJ              |
| 18. Reomol-NF2                   | 40. Reomol-2MP              |
| 19. Diethyl phthalate            | 41. Reomol-2EP              |
| 20. Reomol-EPPX                  | 42. Reomol-2BP              |
| 21. Reomol-2PM                   | 43. Reomol-12J              |
| 22. Reomol-NF2                   |                             |
| (Tributyl phosphate)             |                             |

that the behavior of plasticizers at low temperatures was of importance, but few or no data were available from the literature. Early publications<sup>7</sup> stated that tributyl phosphate, for example, endowed polymers such as cellulose nitrate with "good cold resistance". It was suggested also that the cold-setting point of the plasticizer was of no use in predicting the cold resistance of a product made therefrom. Jordan<sup>8</sup> stated that the viscosity of the plasticizer at room temperature and, for example, its setting point were relationships which had not been established in connection with low-temperature stability.

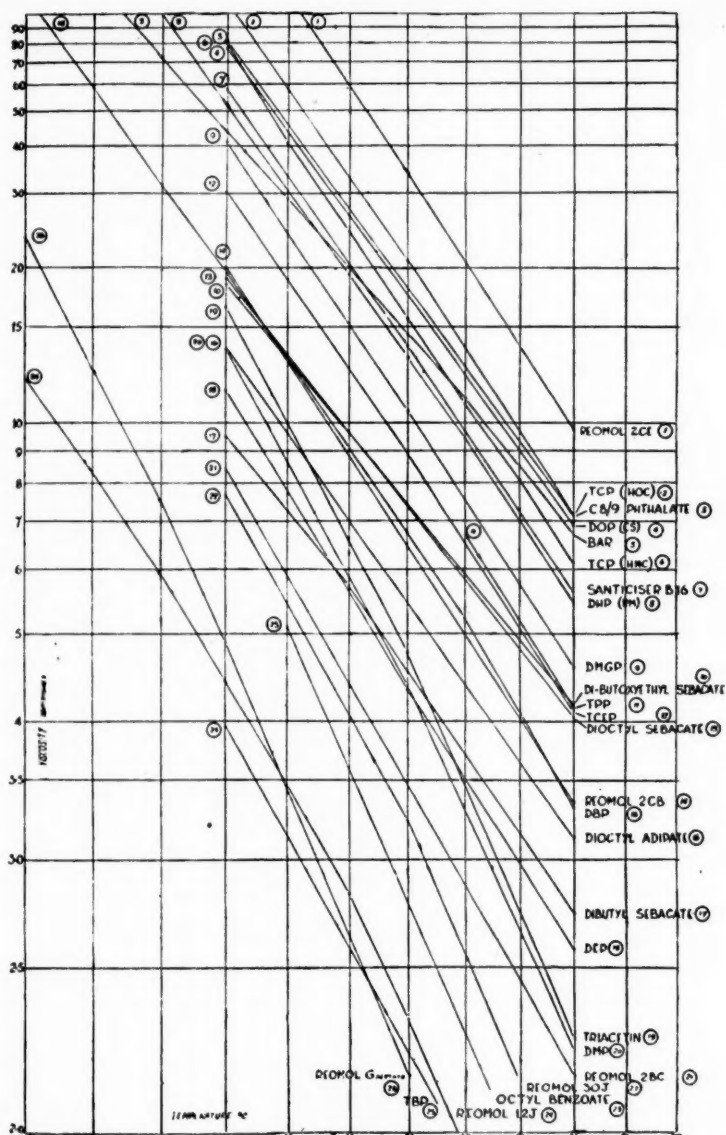


FIG. 12.—Viscosity—Temperature for plasticizers. (See page 204.)

The graph plots  $\log_{10} \nu$  against  $\log_{10} T$  = kinematic viscosity in c.t.s.,  $T$  = absolute temperature. Linearity may be expressed  $\log_{10} \nu = m \log_{10} T + c$  where  $m$  is the slope coefficient.

Plasticizer	$m$	Temp. range	Plasticizer	$m$	Temp. range
Butylacetyl ricinoleate	3.497	60 —20	Santicizer-B16	4.575	80 20
Butoxyethyl sebacate	3.861	80 20	TCP(HOC)	4.660	80 20
Dioctyl sebacate	4.065	80 20	Reomol-12J	4.744	30 —20
TPP	4.213	80 60	TCP(HMC)	4.747	80 20
TCEP	4.251	80 20	DMGP	4.851	80 20
C 8/9 phthalate	4.328	80 20	Reomol-2CE	4.861	80 20
DOP(CS)	4.404	80 20	Reomol-2CB	4.894	80 20
DHP(RM)	4.426	60 —10	DEP	5.093	80 20
Dioctyl adipate	4.505	80 20	DMP	5.955	50 20
DBP	4.549	60 0	Triacetin	6.022	50 20
			Reomol G acetate	6.395	20 —10

In the above values, linearity is assumed between the temperatures specified.

Discussion with workers who had the problem of producing plastics for use at subzero temperatures<sup>9</sup>, showed the belief that it was the extremely fluid nature of tributyl phosphate at low temperatures which made it useful in these respects, but, unfortunately, this plasticizer is not miscible with every polymer and, further, its high volatility restricts its use. Viscosity measurements on this plasticizer down to  $-75^{\circ}\text{C}$  showed that it preserved its fluidity to a remarkable degree and that there was some connection between the plasticizer viscosity at low temperatures and the properties of a plastic made from it.

Two lines of work were started at this stage, namely, measurements of the viscosity of a whole series of plasticizers at low temperatures and the production of plasticizers other than tributyl phosphate, which would have the correct miscibility with other polymers. The results of the low-temperature measurements on a wide range of plasticizers were published early in 1943.

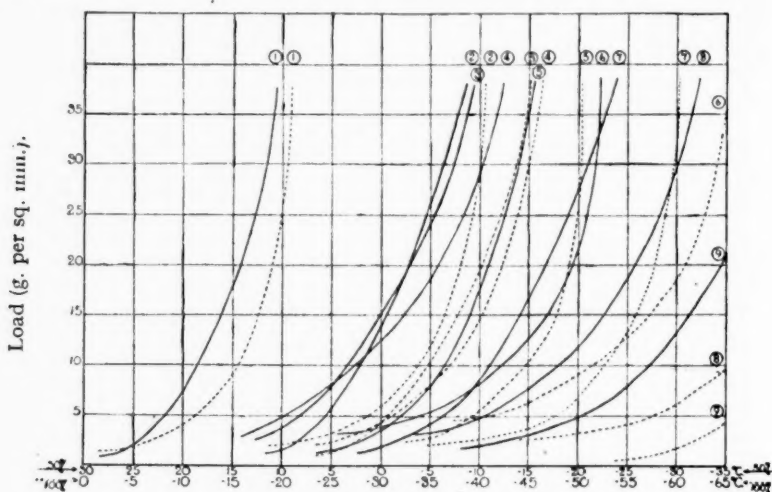


FIG. 13.—Low temperature flexibility tests.

PVC/50% Plasticizer — — — — PVC/100% Plasticizer  
Ordinate common. Abscissae varied.

- |                       |                      |                                 |
|-----------------------|----------------------|---------------------------------|
| 1. Triresyl phosphate | 4. Dioctyl phthalate | 7. { Dibutyl phthalate          |
| 2. Dimethyl phthalate | 5. Dibutyl phthalate | 7. { Triethyleneglycol dioctate |
| 3. Dihexyl phthalate  | 6. Reomol-3BJ        | 8. Tributyl phosphate           |
|                       |                      | 9. Dibutyl adipate              |

Figure 11 shows a number of the viscosity curves. These data were of considerable use in that it enabled good low-temperature plasticizers to be chosen for almost any polymer, but the basic idea arising was an extension of the principle of plasticizer viscosity at low temperatures, in that plasticizer viscosity is applicable to all temperatures of working. Confirmation of these ideas will be found in a paper by Leilich<sup>10</sup>. Unfortunately, no experimental data were quoted in the paper, and all the plasticizers, save one whose viscosity-temperature relations were quoted, were referred to under trade names. The paper was restricted to a consideration of polyvinyl chloride, which is most amenable to these effects as it is a noncrystalline and regular polymer.

Figure 12 shows the viscosity temperature relations of a large number of plasticizers. For simplicity these are shown on the basis of log-log kinematic viscosity against log absolute temperature. The correction factor usually

employed to give linearity at low viscosities has not been included, since this is expected to vary in degree with different classes of plasticizers.

Figure 13 shows the low temperature behavior of two series of polyvinyl chloride compounds prepared by the addition of 50 and 100 per cent of plasticizer, respectively.

Figure 14 shows the low temperature behavior of the series of plasticized Hycar OR-15 compounds given in Table 3.

In both cases a slightly modified form of the well known method of torsional test was used<sup>14</sup>. The results are given in terms of the loading required to twist the ends of the test specimen through an arc of 90° in 5 seconds at the temperature specified.

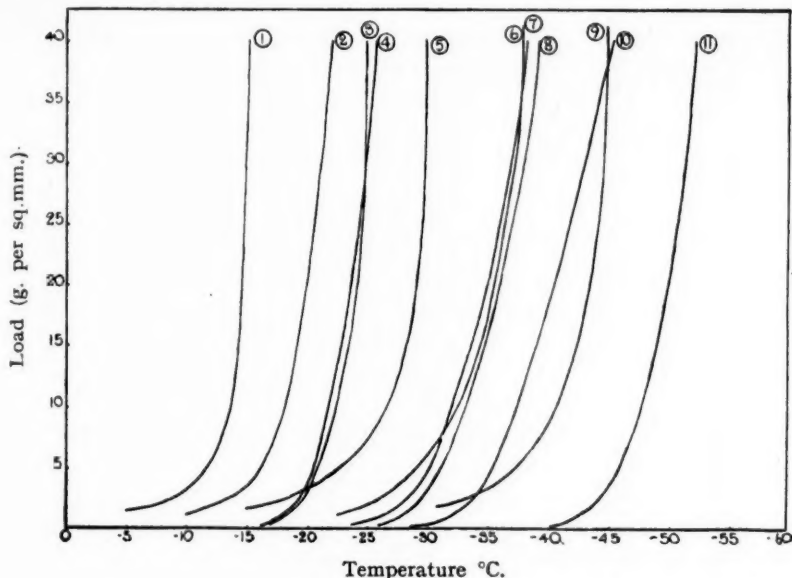


Fig. 14.—Low temperature flexibility tests Hycar OR-15/40% plasticizer.

- |                   |                             |                     |
|-------------------|-----------------------------|---------------------|
| 1. No plasticizer | 5. Glyceryl lactate-acetate | 9. Dibutyl sebacate |
| 2. Reomol-2CE     | 6. D.M.G.P.                 | 10. D.B.P.          |
| 3. T.P.P.         | 7. D.O.P.                   | 11. T.B.P.          |
| 4. T.C.P.         | 8. T.C.E.P.                 |                     |

Figure 15 shows the graphical relationship of the plasticizer viscosity to the low temperature at which the torsional load is 25 g. per sq. mm. cross-section of specimens given in Table 3.

The relationships in these cases are fairly good, although the viscosity-temperature curves of the plasticizers used are not exactly parallel.

Figure 16 shows the connection between the viscosity of the plasticizer and the B.S.S. hardness of polyvinyl chloride compounds made with equal parts of the particular plasticizer.

Figure 17 plots the tensile strength at break of the Hycar OR-15 compounds described in Table 3, thus serving to connect plasticizer viscosity with tensile strength at break in synthetic-rubber compounds. Higher concentrations of plasticizer could reasonably be expected to give curves of a less critical shape,



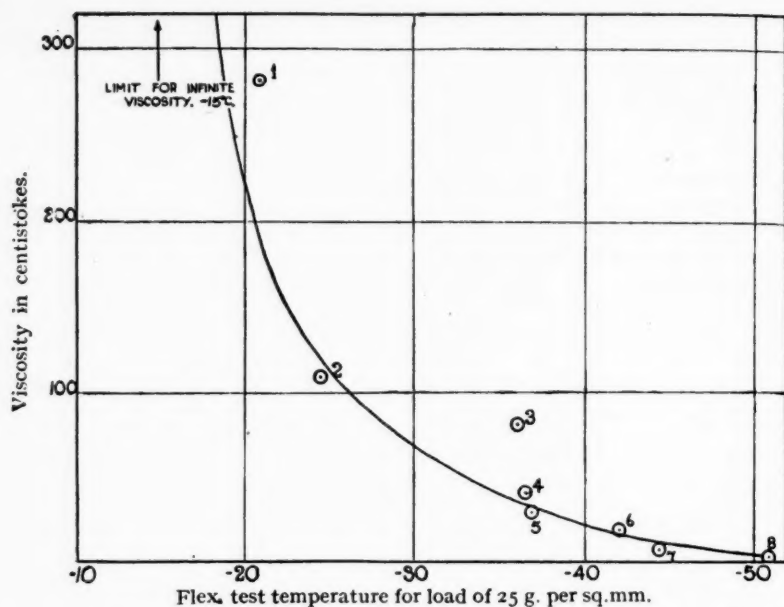


FIG. 15.—Relation between stiffening point of Hycar OR-15 compounds and viscosity of plasticizer.

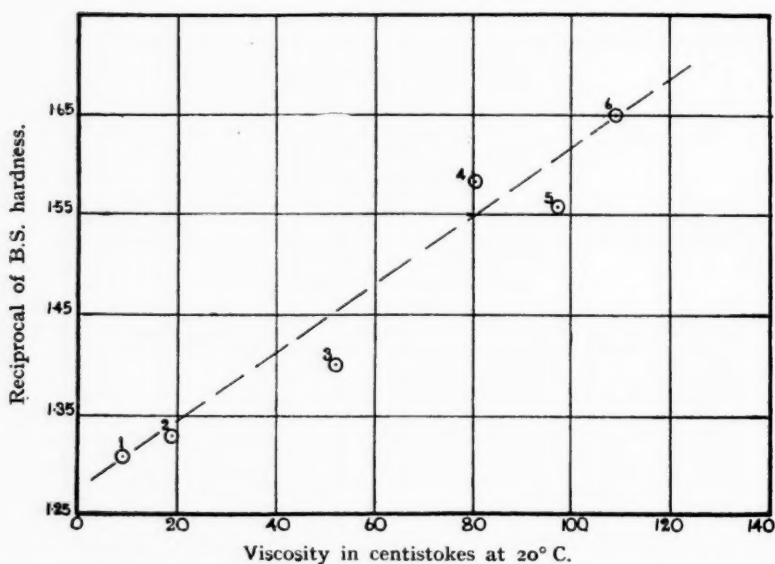


FIG. 16.—Relation between viscosity of plasticizer and hardness of a plastic PVC/100% plasticizer.

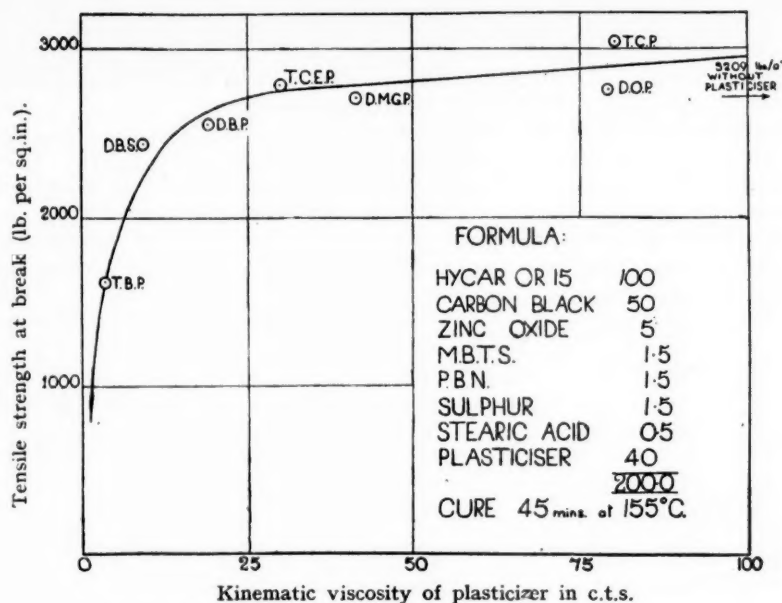


FIG. 17.—Relation between tensile strength and viscosity of plasticizer in Hycar OR-15 compound.

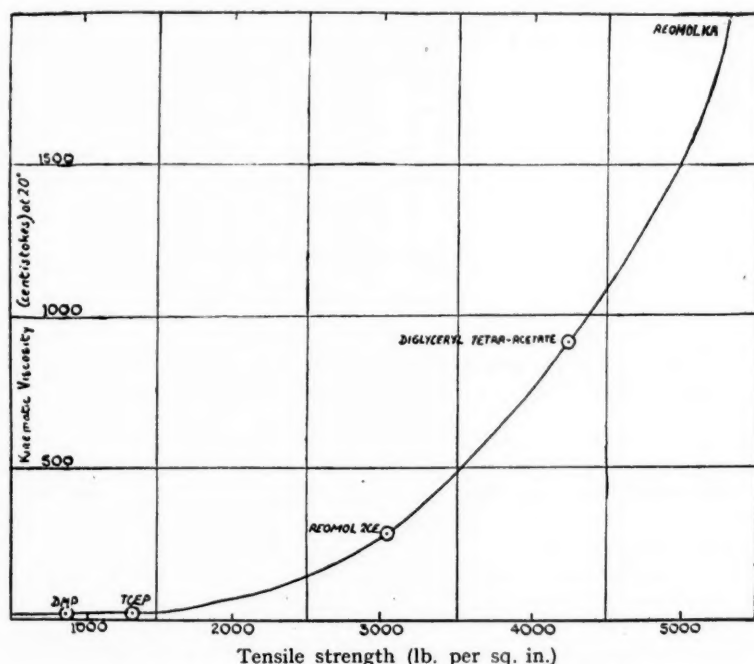


FIG. 18.—Polyvinyl acetate-formal plus 100 per cent plasticizer.

*i.e.*, of lower and more slowly changing tensile strengths. The curves of modulus at break and plasticizer viscosity are also similar to these.

Figure 18 is a further illustration of the connection between plasticizer viscosity and physical properties of plasticized compound. In this case the polymer chosen is Formvar, and the plasticizers used comprise those known to be miscible according to the gelling method quoted in Table 1.

Figure 19 attempts to demonstrate the effect of plasticizer viscosity at room temperature with the electrical properties of polyvinyl chloride compositions. It shows the effect of varying the amount of plasticizer. Curve No. 1 for tricresyl phosphate (TCP) is taken from Würstlin<sup>12</sup>, and shows the variation of specific resistance with percentage composition. The effect of reducing the viscosity of tricresyl phosphate by high *m*-cresylic acids is shown in curve 5.

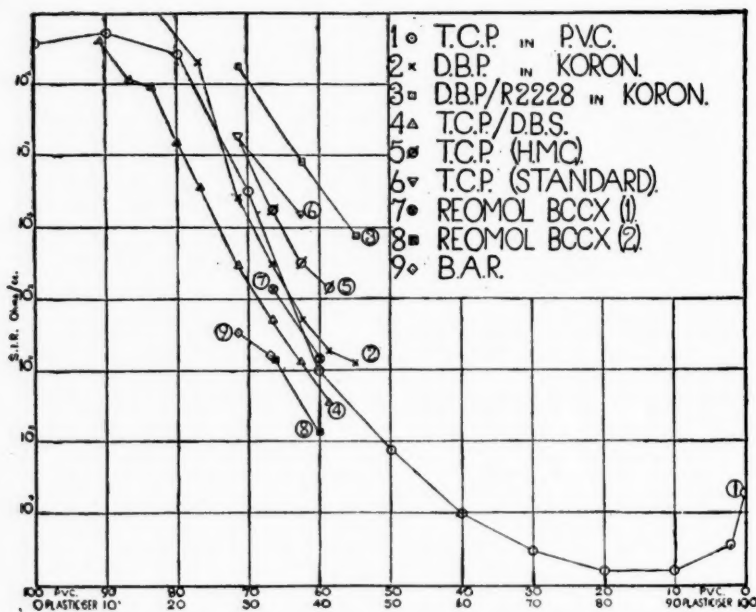


FIG. 19.—Specific resistance of plasticized P.V.C.

Curve 6 shows values for a high *o*-cresyl content in tricresyl phosphate which gives slightly higher values of specific resistance than 5 under similar testing conditions.

The incorporation of mobile dibutyl sebacate (DBS) in equal parts with tricresyl phosphate shows a continued decrease in specific resistance under the same testing conditions as for 5 and 6 and likewise 8 and 9, which show the still less viscous plasticizers, Reomol-CBBX (an alkyl phosphate) and butyl-acetyl vicinoleate (BAR)<sup>13</sup>.

The highest electrical values arise with the most viscous plasticizer, consisting of dibutyl phthalate (DBP) and R-2228 (a high-boiling aromatic distillate) in 50:50 ratio.

Figure 20 uses data of Reed<sup>4</sup>, and shows the relation between plasticizer viscosity and quantity of plasticizer required to give constant modulus in

polyvinyl chloride-acetate compositions. In view of the experimental difficulties in obtaining exactness in such measurements and in view of the fact that Reed obtained the percentage quoted only by interpolating from two concentrations, the spread of the points shown is remarkably narrow. This diagram includes only plasticizers stated by Reed to be miscible with polyvinyl chloride-acetate.

The low-temperature effect is thus not the only one to be strongly influenced by the viscosity of the plasticizer, but tensile strength, hardness, electrical properties and so on can all be markedly controlled by plasticizer viscosity methods.

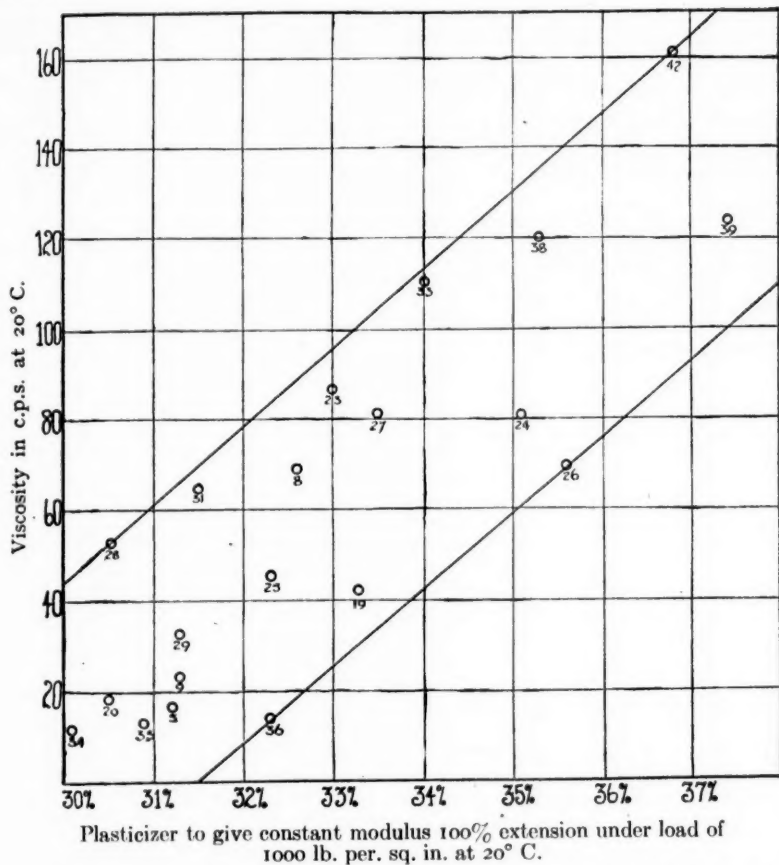


Fig. 20.—Plasticized polyvinyl chloride-acetate relation between viscosity and quantity of plasticizer to give constant modulus at 20° C.

Key to numbered points

- |   |   |
|---|---|
| 5. Triethyleneglycol di-2-ethylhexoate        | 28. Dimethylglycol phthalate                |
| 8. Methylglycolacetate ricinoleate            | 29. Dibutylglycol phthalate                 |
| 9. Methylacetate ricinoleate                  | 31. Butylphthalylbutyl glycolate            |
| 19. Di-2-ethylhexyl acetyl malate             | 33. Tributylglycerol triphthalate           |
| 20. Dibutylglycol sebacate                    | 34. Mixed phthalic and fat acid ester KP150 |
| 23. Di-2-ethylhexyl norcamphene dicarboxylate | 35. Mixed phthalic and fat acid ester KP81  |
| 24. Di-2-ethylhexyl norcamphene dicarboxylate | 36. Tri-2-ethylhexyl phosphate              |
| 25. Di-2-ethylhexyl tetrahydrophthalate       | 38. Tricresyl phosphate                     |
| 26. Dicapryl phthalate                        | 39. Aromatic phosphate M179                 |
| 27. Di-2-ethylhexyl phthalate                 | 42. N-n-butylbenzene sulfonamide            |

Perhaps this is to be expected in view of the fact that the viscosity of the polymer, being a reflection of its molecular weight and shape, is also an indication of its mechanical strength and its flow properties. Here, however, are preliminary data which extend these ideas to plasticized polymers, data on which perhaps it may be possible better to predict the properties of mixtures not previously known and, by the application of mathematical methods, ultimately to obtain exact figures of performance.

#### ACKNOWLEDGMENT

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# EFFECT OF CARBON BLACKS ON THE PHYSICAL PROPERTIES OF NATURAL RUBBER AND NEOPRENE-GN \*

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**INTRODUCTION.**—Carbon black is the most widely used compounding ingredient for both natural and synthetic rubbers. Compounding these rubbers with carbon black enhances the physical properties by increasing tensile strength, hardness, abrasion resistance, and, more markedly, gives easier processing with synthetic rubbers.

Various types of carbon black are manufactured, and an excellent summary of the methods employed has been given<sup>1</sup>. As the largest consumers of rubber are the tire manufacturers, most information on systematic investigations on carbon blacks has been confined to tire stocks.

In recent years, however, aided by the increased usage of synthetic rubbers, it has been realized that rubbers have applications in much wider fields. In particular they are being used more widely as engineering materials, *e.g.*, engine mountings, valves, diaphragms, washers and cables, and in many of these applications other types of carbon black are more suitable than the highly reinforcing channel blacks. Acetylene black, for example, is now widely used to give conducting rubbers<sup>2</sup>, and the softer, low particle size, carbon blacks are being used in resilient mountings.

Recently data have been published<sup>3</sup>, on the use of carbon black in natural rubber and GR-S. The work of Parkinson<sup>4</sup> was of a general nature and demonstrated the relationships between particle size or surface area and specific properties in natural rubber and GR-S. Drogin<sup>1</sup> on the other hand set out to provide basic compounding data on the two rubbers. In the present paper it is intended to give such basic compounding data for both natural rubber and Neoprene-GN, along with a discussion of the varying effects of carbon blacks with the different types of rubbers.

No systematic data on the effect of carbon blacks in Neoprene-GN have yet been published; Drogin<sup>5</sup> has published data only on selected loadings of channel blacks.

To obtain reliable results, a wide range of physical tests was carried out, and repeat mixings were made to enable the errors of test and processing and the correlation between each physical property to be determined by statistical analysis. This aspect of the work has been reported separately<sup>6</sup>.

In general, despite differences in manufacture, the physical properties of the vulcanized rubbers correlate well with the particle size of the carbon blacks.

**EXPERIMENTAL.**—Where standard figures are to be obtained, the work must be repeated if it is to be of any value. It was decided that three repeat mixings would be sufficient.

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To overcome any variations in the raw materials which may introduce an unknown variable into the results, sufficient quantities of each rubber and of each carbon black were blended and kept for these programs. It should be noted that the carbon blacks for both rubbers were not from one common blend, but were separate blends prepared for each series. This was necessary as a time interval of two years occurred between the tests with natural rubber and those with Neoprene-GN.

*Details of Mixes.*—The base mixes used throughout were of the following composition:

Smoked sheet rubber	100	Neoprene-GN	100
Zinc oxide	2.5	Light calcined magnesia	4
Stearic acid	2.0	Stearic acid	1
Sulfur	3.0	Tricresyl phosphate	4
Mercaptobenzothiazole	1.0	Zinc oxide	5

*Vulcanization.*—Preliminary experiments were carried out in natural rubber to determine the optimum cure with the different types and amounts of carbon black. The curves (Figure 1) were constructed, enabling the optimum cure to be selected for any type and amount of carbon black.

In Neoprene-GN, neither the type nor amount of black affected the rate of vulcanization, and the cure selected throughout was 30 minutes at 141° C. It should be understood that these times refer to standard test sheets (approx. 5 mm. thick) and, where thicker samples or heavy moulds were used, appropriate corrections were given to the time of vulcanization.

*Carbon black classification.*—Recently a new classification of carbon blacks has been adopted by American authorities<sup>7</sup>, and the following table gives the class, particle size and specific surface.

TABLE 1

Class	Trade name	Particle size <sup>a</sup> (mu)	Specific surface (sq. m. per g.)	
			(1)	(4)
—	Kosmos-F.4	—	—	—
HPC	Kosmos-T	(ca. 26)	—	105
HMF	Kosmos-40	47	56	45
CF	Shawinigan	43	63	85
SRF	Kosmos-20, S.B. 1	80	33	29
SRF	Magecol lamp black	97	23	23
FT	P-33	91	27	23
MT	Thermax	274	10	19

The following volume loadings were repeated three times in natural rubber:

Thermax, P-33, S.B.I.: 10, 20, 30, 50 volumes.

Magecol: 10, 15, 20, 25, 30, 50 volumes.

Kosmos-T, Kosmos-F.4, Shawinigan: 10, 15, 20, 25 volumes.

In addition two loadings of Kosmos-T (30 and 50 volumes) were evaluated.

The following volume loadings were used in Neoprene-GN:

Thermax: 20\*, 40, 60\*, 80, 100\* and 120\* volumes.

Magecol: 20: 15\*, 30, 45\*, 60 and 75\* volumes.

Kosmos 40: 10\*, 15, 20\*, 30, 40\* and 50\* volumes.

Kosmos T: 10\*, 15, 20\*, 25, 30\*, 40\* and 50\* volumes.

The asterisked loadings were repeated three times, but the remainder were only tested once.

EXPERIMENTAL RESULTS.—*Compounding*.—All milling was carried out on two roll mills having the following characteristics: size, 12 × 6 inches; roll speeds, 26 and 32 r.p.m.; friction ratio, 1:1.23.

With natural rubber, the mill rolls were held as far as possible at 70° C and for Neoprene-GN at 30° C. The temperature of the batch after the addition of

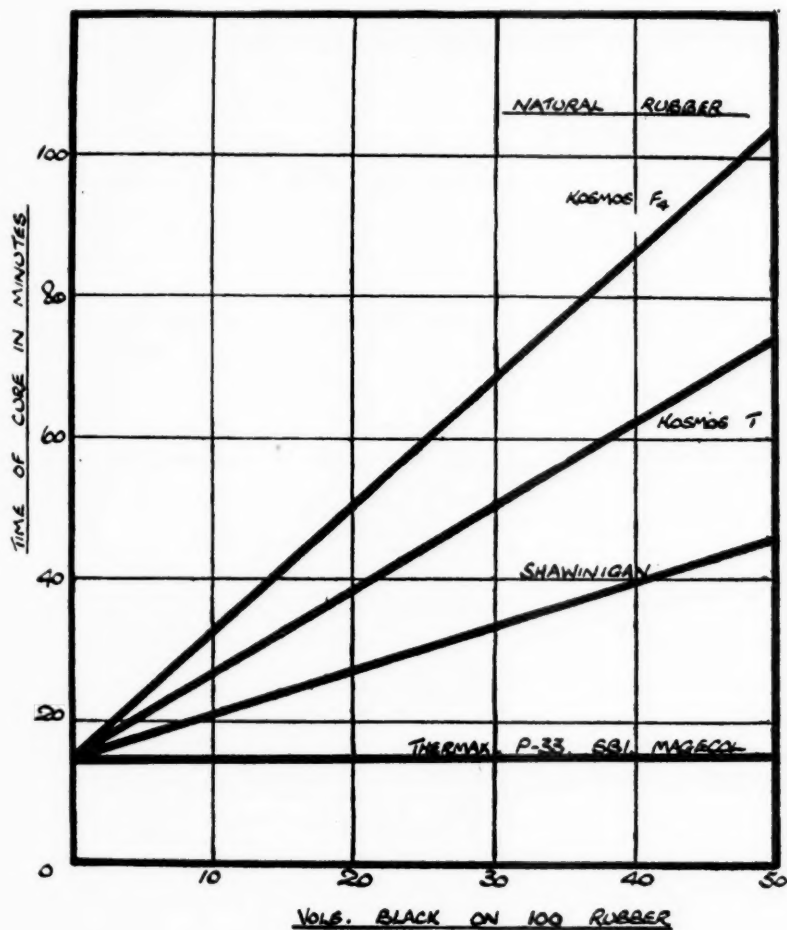


FIG. 1.

the black was noted (Table 2) and in the case of natural rubber the time of incorporation of the carbon black was also recorded (Table 3). For Neoprene-GN all the loadings of black were readily incorporated in under three minutes.

With the exception of Shawinigan black, the ease of incorporation into natural rubber correlates with the particle size of the blacks.

Only small temperature increases are noted with increased black loadings in Neoprene-GN, and in natural rubber no changes occur until the limit of loading is approached, *e.g.*, Kosmos-T and F<sub>4</sub>; 50 and 25 volumes respectively.

TABLE 2  
NATURAL RUBBER  
(Temp. ° C)

Volume loading of black	Kosmos-F.4	Kosmos-T	Shawinigan	S.B.I.	Magecol	P-33	Thermax
10	80-85	70-75	80-85	70-75	80	70-75	—
15	85	75-80	80-85	—	70-75	—	—
20	85-90	75-80	80-85	70-75	75-80	70-75	70-75
25	95	75-80	85	—	70-75	—	—
30	—	80-85	—	70-75	75-80	70-75	70-75
40	—	—	—	—	—	—	—
45	—	—	—	—	—	—	—
50	—	95	—	75-80	80-85	70-75	70-75

## NEOPRENE-GN

	Kosmos-T	Kosmos-40	Kosmos-20	Magecol	Thermax
10	40	40	—	—	—
15	40	40	40	40	—
20	45	45	—	—	45
25	45	—	—	—	—
30	45	48	40	40	—
40	50	48	—	—	45
45	—	—	46	50	—
50	50	50	—	—	—
60	—	—	50	52	50
75	—	—	60	60	—
80	—	—	—	—	50
100	—	—	—	—	50
120	—	—	—	—	50

TABLE 3

## NATURAL RUBBER. Milling time (min.)

Black	10 vols.	15 vols.	20 vols.	25 vols.	30 vols.	50 vols.
Thermax	1.75	—	2.75	—	5	5.75
P-33	2.5	—	3.5	—	5.75	6.5
S.B.I.	2.75	—	3.75	—	6.25	7.75
Magecol	3	3.5	4	4.5	6.5	6.75
Kosmos-T	3.75	4.75	5.75	6.5	7.5	8.25
Shawinigan	6	6.75	9	10	—	—
Kosmos-F.4	10	17	22.5	25.5	—	—

## DISCUSSION

*Tensile Strength* (Figure 2).—All the blacks tested (apart from Kosmos-F.4) in natural rubber pass through a maximum loading value which varies from 40 kg. per sq. cm. to 100 kg. per sq. cm. higher than the value given for the gum compound. Only the finer blacks give this effect in Neoprene-GN, neither Magecol nor Thermax showing any such reinforcement.

The main difference noted between the two rubbers is the broader maximum obtained with Neoprene-GN; in natural rubber it will be seen that P-33 gives values closely similar to S.B.I. except at the actual maxima. Thermax gives higher overall tensile values than lampblack in natural rubber, but these blacks lie together in Neoprene-GN. This difference may be contrasted with that found in GR-S where lampblack gives higher tensile values than Thermax<sup>8</sup>.

*Modulus* (Figures 3, 4).—Magecol lampblack gives a stiffer compound in both Neoprene-GN and natural rubber than would be expected from particle

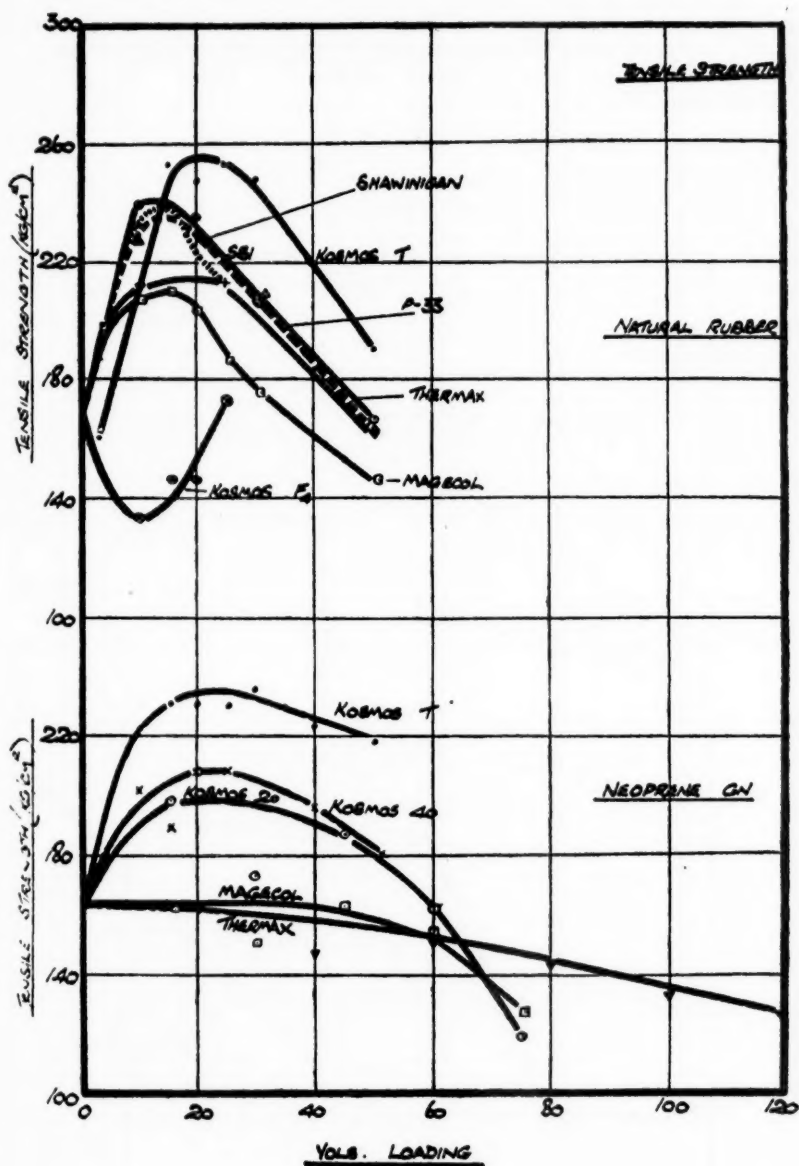


FIG. 2.

size considerations alone. In natural rubber S.B.I. (SRF) at the lower loadings is similar to Kosmos-T, but greater separation occurs in Neoprene-GN.

The main interest lies in comparing the static slow-speed extension and dynamic high-frequency compression moduli. The most notable change is in the position of Kosmos-F.4 in natural rubber, which under dynamic conditions occupies a more correct position with respect to its particle size. The

structure blacks<sup>9</sup>, Shawinigan and Magecol, tend to fall more into line under dynamic high-frequency conditions, but give slightly greater stiffness than could be anticipated from particle-size considerations alone.

These data emphasize the necessity of evaluating carbon black reinforcement under dynamic conditions if such conditions are to be encountered in service.

Correlation of dynamic modulus (Figure 5) with other hardness values, such as British Standard hardness values, show that, in natural rubber, the

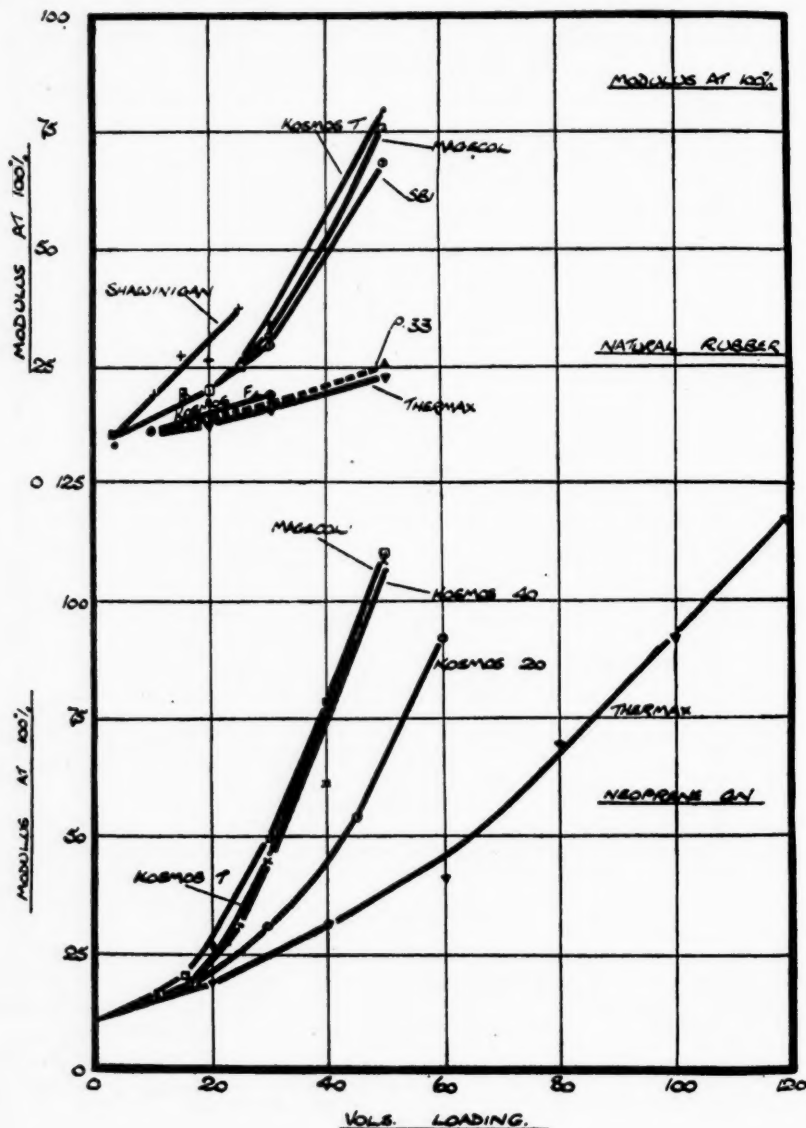


FIG. 3.

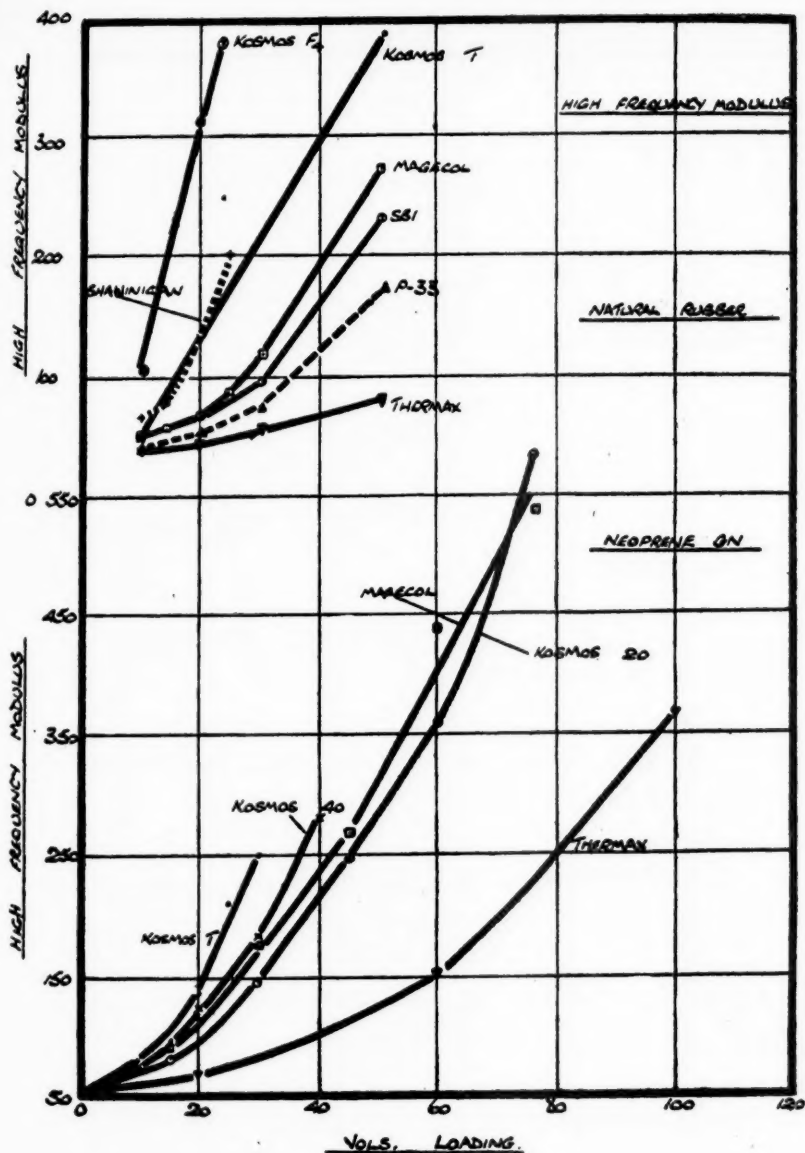


FIG. 4.

blacks give different correlation curves; the finer blacks giving higher dynamic moduli at equivalent B.S. hardness levels. With Neoprene-GN no such separation occurs and one correlation curve is obtained over the whole range of blacks.

**Hardness (Figure 6).**—Curves for British Standard hardness and R.A.B.R.M. hardness are included (Figure 6) as with most compounding work, hardness is the main basis for selection. Broadly the same order of increasing hardness is obtained for B.S. hardness as was noted for dynamic modulus.



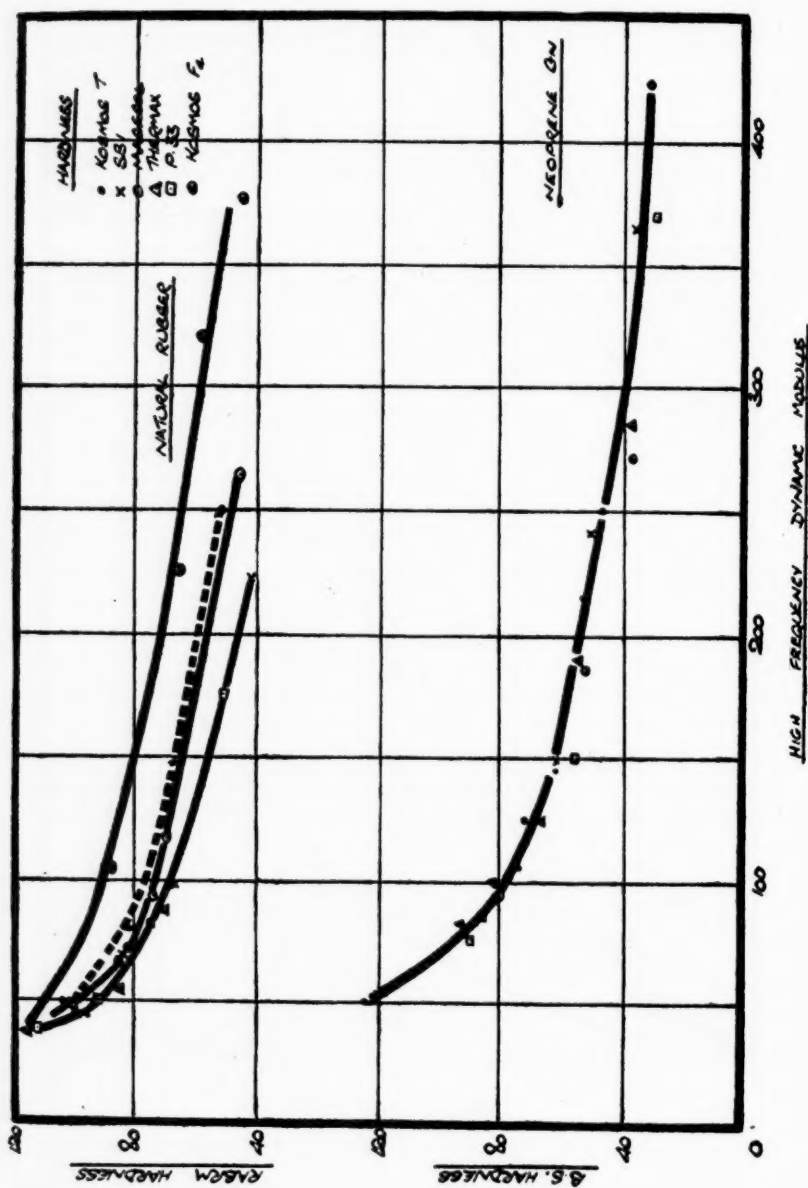


FIG. 5.

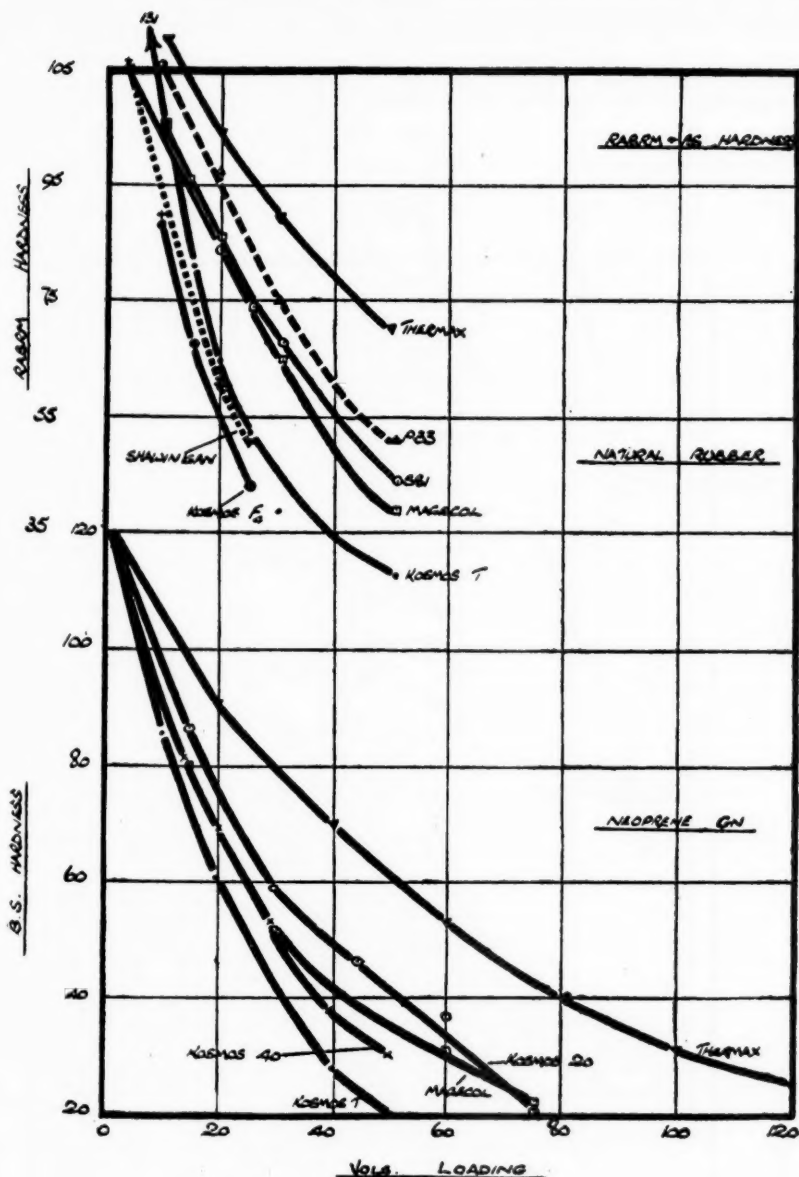


FIG. 6.

It will be seen from Tables 6-7 that the correlation of Shore hardness and B.S. or R.A.B.R.M. hardness varies slightly according to the black used. This point was not dealt with in Users Memorandum U-8<sup>10</sup>. The R.A.B.R.M. figures were obtained in 1940 before the B.S. hardness was widely adopted.

The Shore hardness values given in this paper for natural rubber were obtained on a Shore durometer which had not been calibrated<sup>10</sup>. To obtain the

"correct" values the results given here should be increased by about eight points. We have not corrected the values as the original values were used for statistical calculations which are reported elsewhere<sup>6</sup>.

*Plasticity (Williams')* (Figure 7).—With both natural rubber and Neoprene-GN, the recovery values fall into more or less the same order as the compression values and, therefore, it is probably only necessary to use com-

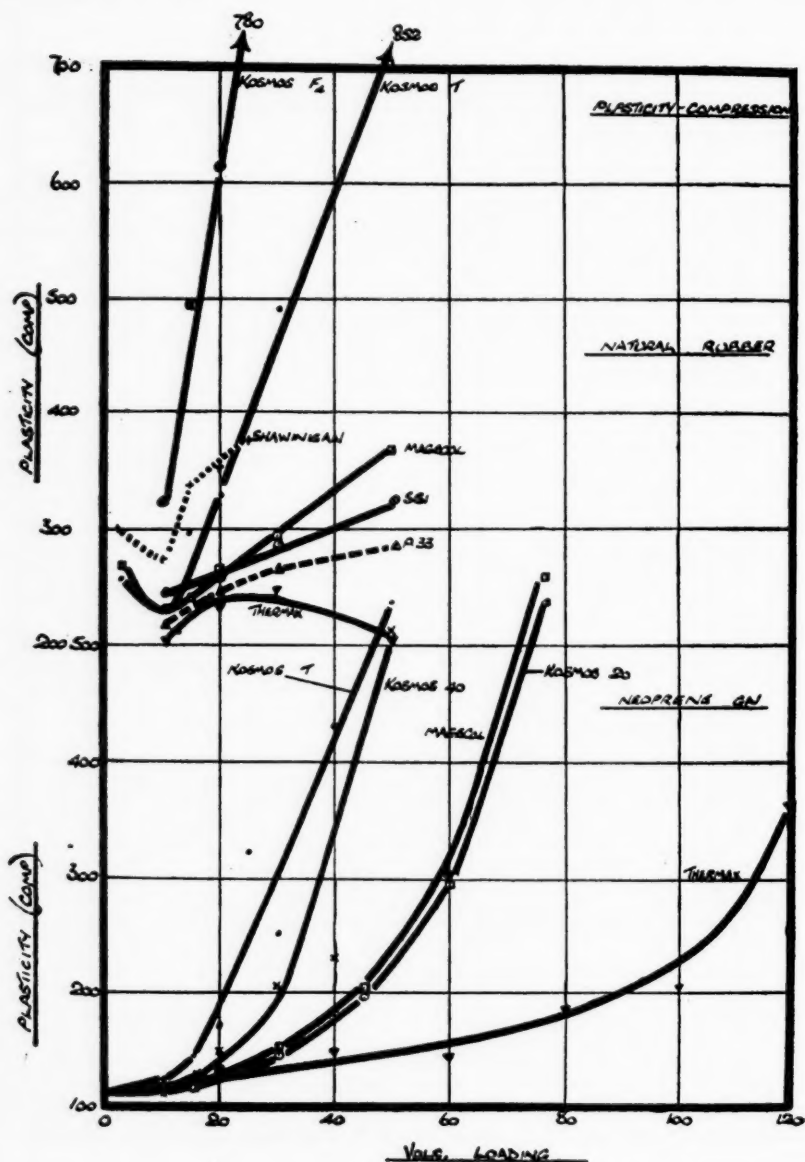


FIG. 7.

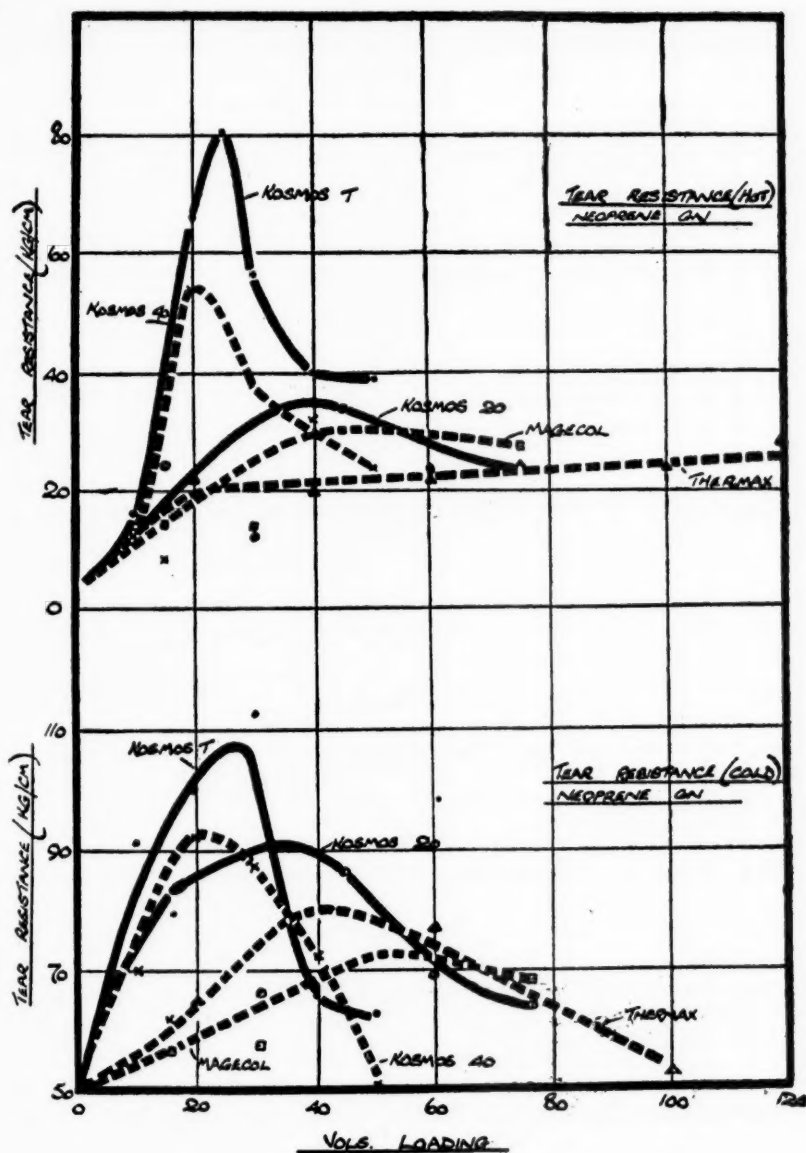


FIG. 8.

pression values when studying a single polymer. In a comparison of different rubbers it is necessary to include recovery measurements, as for a given value of plasticity (compression) different recovery values can be obtained.

The behavior of lampblack in Neoprene-GN is worthy of comment, as over the whole loading range, plasticity values are very similar to Kosmos-20, and yet up to a 60-volume loading, markedly harder vulcanizates are obtained

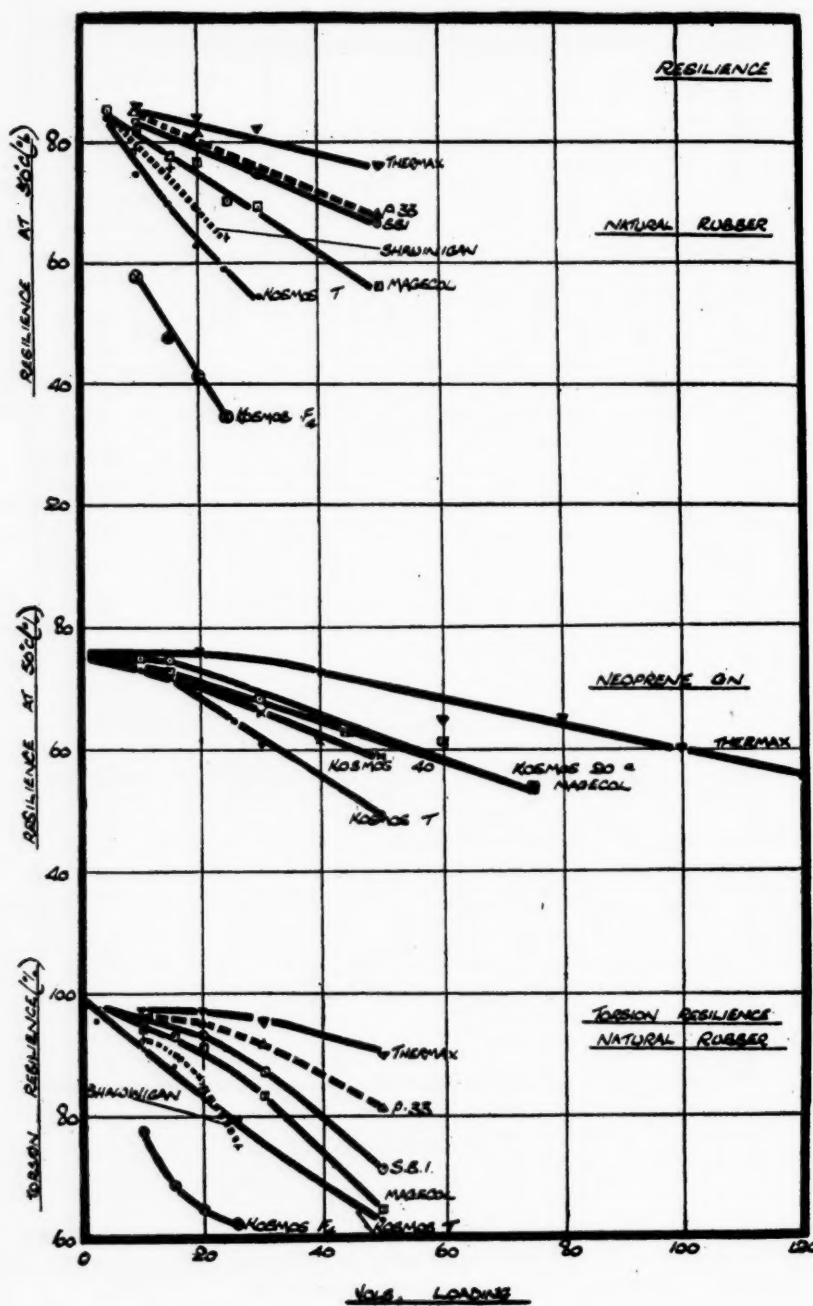


FIG. 9.

(Figure 6). Otherwise the general order of results are very similar to those obtained for B-S-hardness.

*Tear Resistance* (Figure 8).—Tear resistance results are only available for the Neoprene-GN compounds as this test was not carried out on the natural rubber compounds. The most important point arising out of these tests is that as the particle size decreases, so does the "peakiness" of the curve increase. This is particularly noticeable at the higher temperature of testing, where the

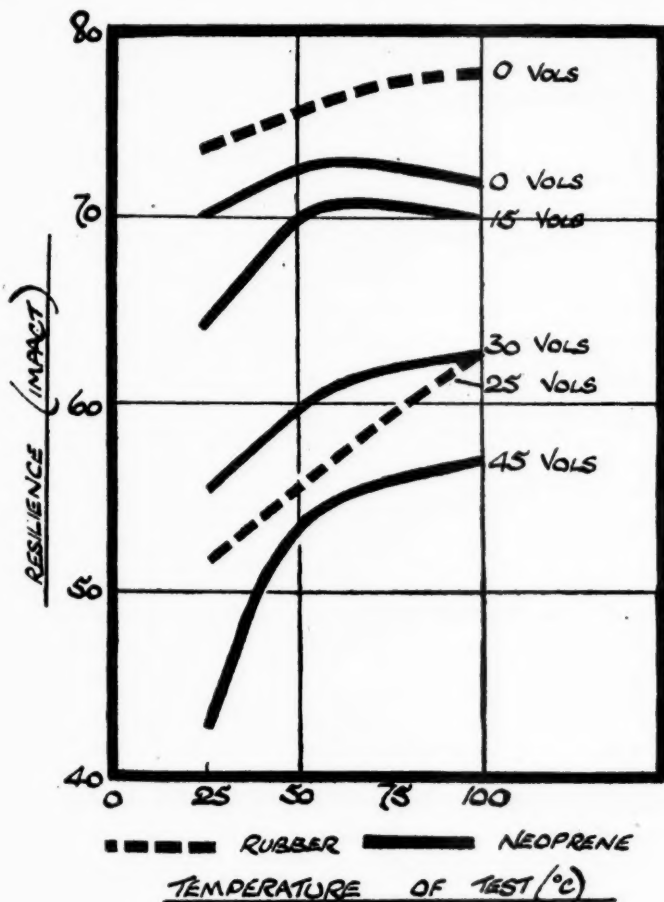


FIG. 10.

results for Thermax (large particle size) remain practically constant over the whole loading range; Magecol and Kosmos-20 (medium particle size) show a slight rise to an optimum value, whereas Kosmos-T and Kosmos-40 (fine particle size) show a very marked peak. The second point arising out of these tests is the outstanding high optimum resistance to tearing imparted by Kosmos-T.

*Resilience (Impact and Torsion)* (Figures 9, 10).—In natural rubber there is no difference in the relative order of the blacks, when tested by either impact



or torsion, apart from a cross over at 20 volumes with Shawinigan and Kosmos-T. There is practically a straight line correlation in natural rubber between these two methods of test; torsion test results are slightly higher. Other evidence<sup>11</sup> has indicated that differences exist between different polymers. There is less separation between blacks in Neoprene-GN than in natural rubber and the rate of fall in resilience with black loading is slower in Neoprene-GN than in natural rubber. This is more marked as the particle size of the black decreases.

As has been remarked in other sections of this discussion, the behavior of lamp black differs in these two rubbers. In natural rubber, lampblack falls between Kosmos-T and S.B.I., whereas in Neoprene-GN it is identical with Kosmos-20 and tends to give higher resilience values than Kosmos-20 for an equivalent hardness.

Comparison of P-33 and S.B.I. in natural rubber reveals that under dynamic conditions P-33 gives consistently higher resilience values, although under impact conditions, the curves are almost identical. Neoprene-GN shows marked thermoplasticity at the higher temperatures of testing and until relatively high black loadings are used, impact resilience shows a sharp fall at 100° C compared to the values obtained at 50° C.

Increasing black loadings lead to an increase in temperature sensitivity and Figure 10 illustrates this effect with both Neoprene-GN and natural rubber. Within the temperature range studied no thermoplasticity is evidenced by natural rubber, although a very marked dependence on temperature is noted with a loading of 25 volumes of Kosmos-T.

**Abrasion Tests** (Figures 11, 12).—These may best be considered under two headings: (1) Dunlop abrasion machine, and (2) du Pont abrasion machine.

(1) Only a limited range of black loadings were covered (Figure 11) in Neoprene-GN, but all show a maximum resistance to abrasion. This maximum occurs at about 30 volumes loading with Kosmos-T and Kosmos-40, about 45 volumes with Kosmos-20 and Magecol, and 25 volumes with Thermax. The position of Magecol is more in agreement with particle size, but the values obtained with Kosmos-40 are of considerable interest, giving results of the same order as Kosmos-T.

(2) Comparison with the du Pont abrasion data (Figure 12) show that, although a similar order of merit is obtained, there is no similarity in the effect of black loading. In Neoprene-GN, within the limits tested, increasing amounts of black lead to further improvements in resistance to abrasion. In natural rubber a maximum is reached with Kosmos-T at 30 volumes. With the exception of Thermax, which remains at a steady value, the remainder of the blacks give increased resistance to abrasion with increased black loadings.

In both rubbers, du Pont abrasion values correlate well with hardness, a more or less linear correlation existing for each black. Exact correlations between hardness tests and du Pont abrasion have been calculated from the results given in this paper and are reported separately<sup>6</sup>. It was found that abrasion resistance as measured on the du Pont machine could be explained to an extent of 80 per cent by hardness and tensile alone. It has also been shown that, while both abrasion tests are mainly functions of hardness and tensile strength, the proportion of these properties which make up the two abrasion tests are quite different. This is to be expected as the rubber is not allowed to relax in the du Pont abrasion test, whereas it is with the Dunlop abrasion machine.

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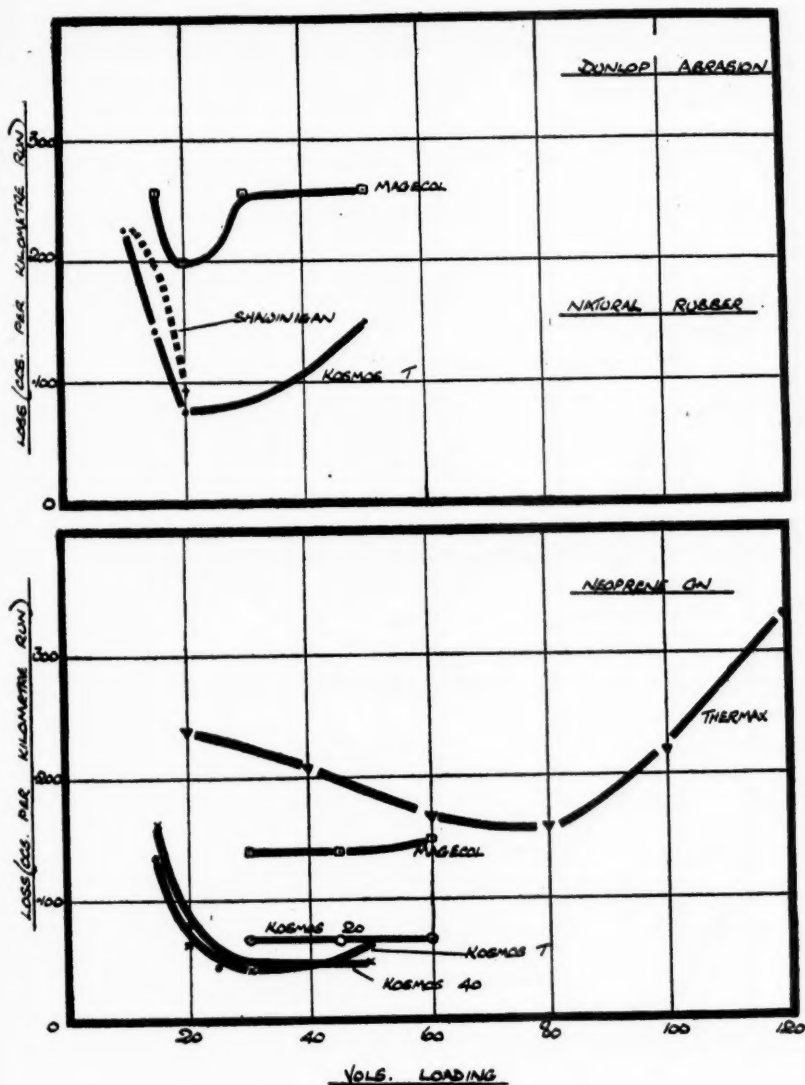


FIG. 11.

*Other Tests.*—Swelling in benzene does not differentiate greatly between blacks. In natural rubber Therman and P-33 give slightly greater swelling at equivalent volume loadings than the remainder (Magecol-Kosmos-T). This effect is reproduced in Neoprene-GN, the curve for Therman lying away from the remainder. The results obtained with Neoprene-GN show that there is a good correlation between swelling in benzene and modulus. This correlation is illustrated in Figure 13. The correlation is not so good for natural rubber, and some of this variation may be in part due to variations in the state of cure. It has been stated<sup>12</sup> that the higher the combined sulfur content, the

less becomes the swelling in benzene. The addition of fillers upsets the rate of vulcanization and hence affects the rate of combination of sulfur. Vulcanization to a constant combined sulfur value would be required rather than the usual estimation of optimum cure by physical property changes.

Detrition (or heat build-up) tests under constant load generally follow resilience changes within each rubber, but different correlations exist from rub-

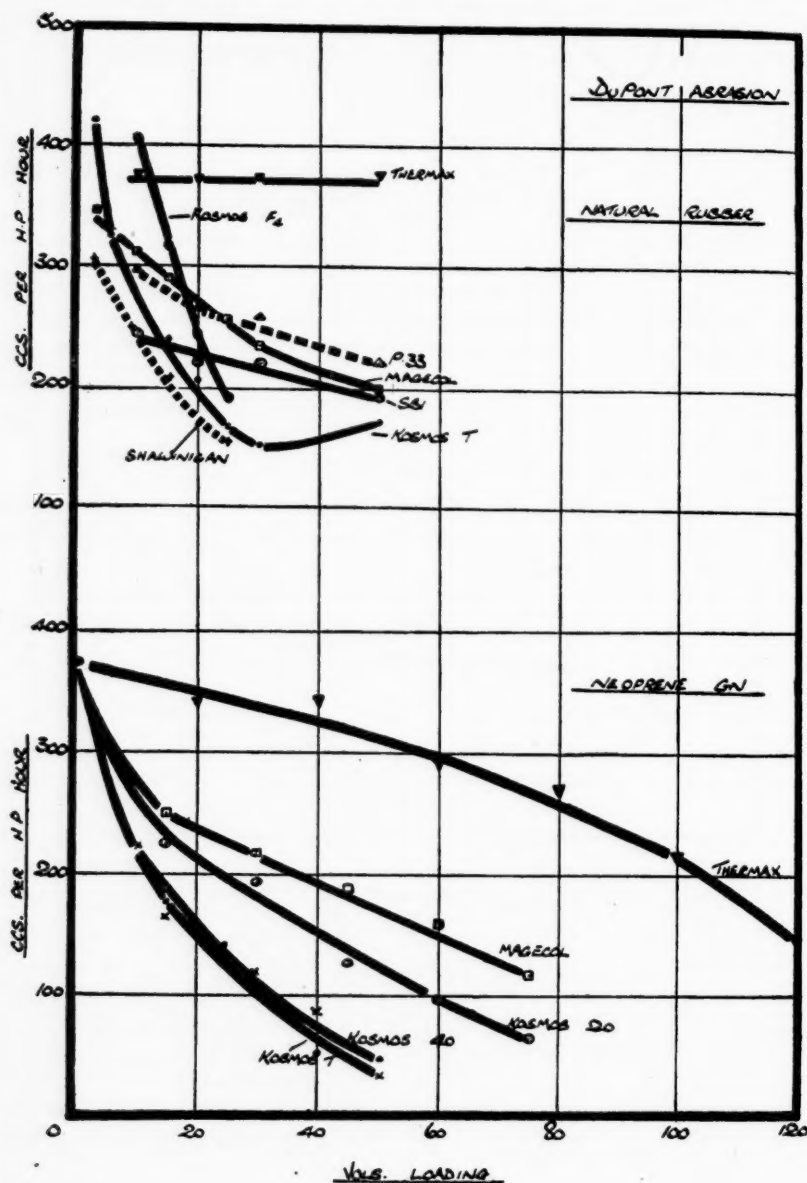


FIG. 12.

ber to rubber. In fact it has been shown<sup>6</sup> that there is a negative correlation with natural rubber and a positive correlation with Neoprene-GN. This means that with natural rubber if the hardness is maintained constant and resilience increased the heat build-up decreases, whereas with Neoprene-GN, under the same conditions, the heat build-up increases.

The 25-kilogram load, with highly loaded stocks on the Schopper-Martens test, may not be sufficient to deform the sample appreciably and therefore low heat build-up results are obtained. Some of the natural rubber results indicate that this is so, for the 25-kilogram load results flatten off with increasing black loading, whereas the 50-kilogram load results go on increasing with

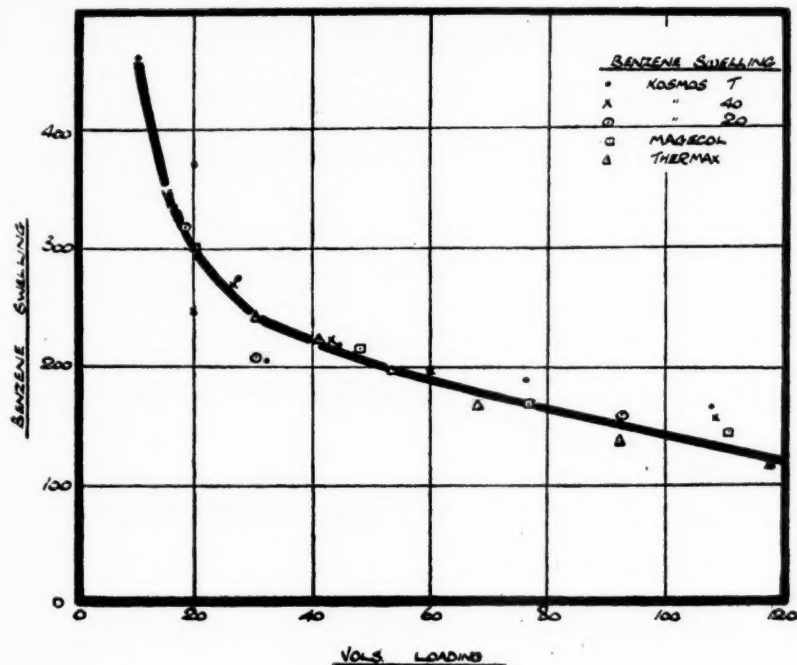


FIG. 13.

loading. To obtain a more accurate comparison it would be better to carry out the test under conditions of constant deformation rather than constant load.

Compression-set measurements<sup>13</sup> were carried out on the Neoprene-GN series, and it is of interest to note that under conditions of constant deformation no change in set occurs over the whole range of loadings. The opposite effect is found with Perbunan<sup>14</sup> where the compression set increases as the loading of channel black is increased. By giving an eightfold overcure to Neoprene-GN the compression set can be improved and made comparable to that of natural rubber<sup>15</sup>.

**Comparison of Blacks.**—Table 4 has been drawn up showing the relative position of each black for each physical property and this table gives a clear picture of the relative merits of each black when a selection for a particular property or group of properties is made.

TABLE 4  
NATURAL RUBBER

	1	2	3	4	5	6	7
<i>A. Rupture Tests (→increasing)</i>							
Tensile strength	Kosmos-F.4	Magecol	Thermax	P-33	Shawinigan	S.B.I.	Kosmos-T
Elongation	Shawinigan	Magecol	(Kosmos-F.4*)	S.B.I.	Kosmos-T	Thermax	P-33
<i>B. Non-Rupture Tests. Hardness and stiffness tests (→increasing)</i>							
Modulus	Thermax	P-33	(Kosmos-F.4*)	S.B.I.	(Magecol —	Kosmos-T	Shawinigan
Dynamic modulus	Thermax	P-33	S.B.I.	Magecol	Shawinigan	Kosmos-T	Kosmos-F.4
High-frequency modulus	Thermax	P-33	S.B.I.	Magecol	Shawinigan	Kosmos-T	Kosmos-F.4
Indentation	Thermax	P-33	S.B.I.	Magecol	Kosmos-T	Kosmos-F.4	Shawinigan
Shore hardness	Thermax	P-33	S.B.I.	Magecol	Kosmos-T	Kosmos-F.4	Shawinigan
R.A.B.R.M. hardness	Thermax	P-33	S.B.I.	Magecol	Kosmos-T	Shawinigan	Kosmos-F.4
Plasticity compression	Thermax	P-33	S.B.I.	Magecol	Kosmos-T	Shawinigan	Kosmos-F.4
<i>C. Non-Rupture Tests. Resilience (→increasing)</i>							
Resilience (tripsometer)	Kosmos-F.4	Kosmos-T	Shawinigan	Magecol	S.B.I.	P-33	Thermax
Dynamic resilience	Kosmos-F.4	Kosmos-T	Shawinigan	Magecol	S.B.I.	P-33	Thermax
Torsional resilience	Kosmos-F.4	Kosmos-T	Shawinigan	Magecol	S.B.I.	P-33	Thermax
<i>D. Other Non-Rupture Tests (→increasing)</i>							
Swelling benzene	Shawinigan	(S.B.I. —	Kosmos-T —	Magecol)	P-33	Thermax	Kosmos-F.4
<i>E. Service Tests (→increasing)</i>							
du Pont abrasion resistance	Thermax	P-33	Magecol	S.B.I.	Kosmos-F.4	Kosmos-T	Shawinigan
Detrition	Thermax	S.B.I.	P-33	Magecol	Shawinigan	Kosmos-T	Kosmos-F.4

\* Difficult to assess position—see table.

TABLE 5  
RELATIVE ORDER OF RESULTS

NEOPRENE GN

	1	2	3	4	5
<i>Rupture Tests (→increasing)</i>					
Tensile strength	(Thermax —	Magecol)	Kosmos-20	Kosmos-40	Kosmos-T
Elongation	Kosmos-40	Kosmos-T	Magecol	Kosmos-20	Thermax
Tear—Cold	Magecol	Thermax	(Kosmos-20 —	Kosmos-40)	Kosmos-T
Hot	Thermax	Magecol	Kosmos-20	Kosmos-40	Kosmos-T
<i>Non-Rupture Tests Hardness or Stiffness (→increasing)</i>					
Modulus (100%)	Thermax	Kosmos-20	Magecol	(Kosmos-T —	Kosmos-40)
High-frequency modulus	Thermax	Kosmos-20	Magecol	Kosmos-40	Kosmos-T
Shore hardness	Thermax	Kosmos-20	Magecol	Kosmos-40	Kosmos-T
B.S.I. hardness	Thermax	Kosmos-20	Magecol	Kosmos-40	Kosmos-T
Plasticity (compression)	Thermax	(Kosmos-20 —	Magecol)	Kosmos-40	Kosmos-T
<i>Non-Rupture Tests (→increasing)</i>					
Swelling (benzene)	(Magecol —	Kosmos-40 —	Kosmos-T)	Kosmos-20	Thermax
Resilience (tripsometer)	Kosmos-T	Kosmos-40	(Kosmos-20 —	Magecol)	Thermax
Abrasion (du Pont)	Thermax	Magecol	Kosmos-20	Kosmos-40	Kosmos-T
Abrasion (Dunlop)	Thermax	Magecol	Kosmos-20	Kosmos-40	Kosmos-T

The order of carbon blacks as set out in Tables 4 and 5 enables some generalizations to be made, although in certain cases these may have to be restricted.

Both Magecol and Shawinigan in natural rubber, and the former in Neoprene-GN give anomalous results. This has been attributed to the structure forming<sup>9</sup> properties of these blacks. These anomalies occur largely with hardness and resilience, Magecol generally gives harder products than Kosmos-20 or S.B.I. (SRF types), and lower resilience values. Shawinigan varies slightly in that with indentation or tensile stiffness measurements it gives higher relative hardness values than its particle size warrants, but assumes a correct position under dynamic tests. In all resilience measurements it occupies a correct position in relation to particle size.

TABLE 6

50° Shore	Thermax	P-33	S.B.I.	Magecol	Shawinigan	Kosmos-T	Kosmos-F.4
Volume loading	35	26	18	15	105	13.5	12
Tensile strength	191	223	236	210	233	240	137
Elongation	525	655	565	560	595	615	615
Modulus (300%)	71	43	74	71	62	62	34
R.A.B.R.M. hardness	85	86	86	95	89	89	80
Resilience triposometer (50° C)	79.5	78	80.5	77.5	78.5	68.5	52.5
Detrition (° C)	64	71.5	70	78	80	102	181
du Pont abrasion	—	261	224	290	238	255	>320
Plasticity							
Compression	255	260	255	243	285	275	400
Recovery	250	265	265	270	330	355	460
60° Shore							
Volume loading	57.6*	45	32	25	16	20	19.5
Tensile		173	203	187	236	255	145*
Elongation		500	425	490	520	585	630
Modulus (300%)		80	138	101	96	78	34
R.A.B.R.M. hardness		57	65	74	72	67	58
Resilience triposometer (50° C)		69.5	74.5	71.5	73.0	64.0	40.5
Detrition (° C)		75	68	77	82	116	189
du Pont abrasion		232	217	250	195	191	252
Plasticity							
Compression		275	200	285	350	325	625
Recovery		300	300	300	415	400	700
70° Shore							
Volume-loading	75*	61*					
Tensile			455	37	27	30	28
Elongation			174	163	200	249	191*
Modulus (300%)			300	335	420	475	640*
R.A.B.R.M. hardness			195*	160*	150*	132	48*
Resilience triposometer (50° C)			47.5	53.5	49	39	34
Detrition (° C)			68.0	64.0	62.0	53.0	32.0
du Pont abrasion			69	75	86	130	
Plasticity			199	216	153	153	
Compression			315	315	385	485	850*
Recovery			330	330	470	550	

\* Extrapolated.

Otherwise the blacks conform to the general principle where decreasing particle size gives greater stiffness and lower resilience.

Rupture tests (tensile and tear) do not conform with this neat picture, for Magecol has relatively low tensile values in both rubbers. With Kosmos-F.4 in natural rubber, the low tensile values may be due to both the difficulty of obtaining a good dispersion and the effects of the black on the degree of vulcanization.

In the du Pont abrasion test both Shawinigan and Kosmos-F.4 give anomalous results in natural rubber, but the remaining blacks including Magecol are correctly placed in relation to particle size in both rubbers. The results ob-



tained on the Dunlop machine give the correct order in both Neoprene-GN and natural rubber.

From the foregoing discussion and Tables 4 and 5 it is clear that if the hardness is increased by changing the black or increasing the amount of black part of the resilience must be sacrificed. For this reason a careful selection must be made, and the data in this report provide a useful basis for any such selection.

The data can be abstracted in several ways, depending on the particular use in mind. Most compounding is carried out on a basis of specific hardness and it is, therefore, logical to compare blacks at constant hardness levels and this has been done in Tables 6 and 7.

TABLE 7

75 B.S. Hardness	Kosmos-T	Kosmos-40	Kosmos-20	Magecol	Thermax
Volume loading	15	175	20.5	17	34
Parts per 100 parts Neoprene	22.5	26	31	25.5	51
Tensile (kg. per sq. cm.)	233	210	200	160	155
Elongation (%)	750	600	630	660	560
Modulus at 100%	20	20	20	20	25
High-frequency modulus	110	110	100	100	100
Resilience at 50° C (%)	71	72	72.5	73	74
Shore hardness	60	60	60	56	56
Abrasion—du Pont	180	180	210	250	230
Dunlop	.130	.120	—	—	.220
Tear—Cold (kg. per cm.)	95	85	85	60	75
Hot (kg. per cm.)	20	30	25	15	25
Plasticity (compression)	140	130	120	120	130
Swelling in benzene	300	280	280	280	265
50 B.S. Hardness					
Volume loading	25	31	39.5	30.5	64
Parts per 100 parts Neoprene	37.5	47	59	46.5	95.5
Tensile (kg. per sq. cm.)	235	210	190	190	150
Elongation (%)	520	350	390	440	350
Modulus at 100%	30	45	40	40	50
High-frequency modulus	200	200	200	180	170
Resilience at 50° C (%)	65	66	65	69	69
Shore hardness	71	72	72	70	67
Abrasion—du Pont	135	135	150	215	280
Dunlop	.040	.040	.070	.140	.160
Plasticity (compression)	200	200	170	150	160
Tear—Cold (kg. per cm.)	105	85	85	65	75
Hot (kg. per cm.)	80	35	30	20	20
Swelling in benzene	240	215	210	220	195
30 B.S. Hardness					
Volume loading	39	50	66	60	101
Parts per 100 parts Neoprene	58.5	75	97	90	152
Tensile (kg. per sq. cm.)	225	180	150	150	135
Elongation (%)	300	150	150	160	180
Modulus at 100%	75	110	115*	110	95
High-frequency modulus	—	—	440	410	370
Resilience at 50° C (%)	56	58	57	60	60
Shore hardness	80	81	85	85	82
Abrasion—du Pont	70	45	85	150	220
Dunlop	.045	.050	—	.150	.230
Plasticity (compression)	400	500	370	321	210
Tear—Cold (kg. per cm.)	70	45	70	70	50
Hot (kg. per cm.)	40	25	25	30	25
Swelling in benzene	190	160	150	150	135
(%-volume)					

\* Extrapolated.

TABLE 8  
NATURAL RUBBER

	Thermax					P-33					S.B.I.					Magnecol				
	10	20	30	50	100	10	20	30	50	100	10	20	30	50	100	10	20	30	50	100
Volume loading	211	217	204	182	228	233	211	167	240	235	208	168	108	202	250	31	108	210	15	20
Tensile strength	698	670	573	424	715	713	608	482	648	552	451	264	168	540	688	688	633	557	292	202
Elongation	12	15	16	15	15	13	18	23	14	21	30	69	16	14	21	14	21	21	21	21
Stress strain 100%	19	19	30	55	20	22	31	53	25	44	75	136	16	47	26	16	27	47	47	47
Stress strain 200%	28	37	60	100	29	32	53	90	44	85	130	164	24	47	26	16	27	47	47	47
Stress strain 300%	44	65	108	150	46	52	89	135	75	135	198	164	24	47	26	16	27	47	47	47
Stress strain 400%	73	108	150	—	77	92	141	190	126	201	—	—	—	—	—	—	—	—	—	—
Stress strain 500%	133	162	—	—	154	148	190	—	—	—	—	—	—	—	—	—	—	—	—	—
Stress strain 600%	38	45	48	56	39	47	52	63	42	53	59	74	41	43	50	53	60	61	53	53
Shore hardness	118	103	90	70	115	97	75	57	62	84	67	44	113	105	95	85	74	64	38	38
R.A.B.R.M. hardness	95	96	—	77	95	95	—	67	96	95	—	53	—	—	—	96	96	88	70	46
S.E.	84.1	83.0	80.9	76.8	83.9	80.4	75.9	67.3	83.2	79.8	75.7	66.1	84.9	81.2	76.7	76.1	70.0	89.8	56.0	56.0
Resilience 50° C	14.8	14.5	13.7	12.4	14.1	13.9	13.2	10.9	14.2	13.1	12.2	9.8	15.2	13.9	13.6	13.0	12.1	11.7	9.5	9.5
Indentation	2	6	5	11	3	5	6	12	4	6	10	19	14	6	6	7	13	12	13	12
Permanent set 300° C	374	365	370	373	292	263	260	224	241	220	220	190	344	308	290	263	250	232	195	195
du Pont abrasion	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dunlop abrasion	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Benzene swelling 25° C	340	296	260	212	335	299	259	209	308	258	204	162	365	313	285	252	244	211	166	166
2 days	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Deterioration (° C) 1,000 revs.	70	67	65	62	73	72	72	78	70	68	69	68	74	77	78	78	77	75	78	78
25 kg.	99	87	95	98	105	108	113	128	103	108	106	113	88	111	118	122	120	129	129	129
50 kg.	90.6	89.4	87.8	83.3	90.0	86.0	81.4	69.7	89.5	85.0	81.3	71.0	—	—	—	87.4	84.3	80.2	77.9	64.7
Dynamic resilience	42.0	49.3	57.8	76.6	43.7	52.8	67.8	105.3	48.3	61.6	80.7	129.7	—	—	—	49.2	57.3	64.8	84.9	86.2
Dynamic modulus	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
High frequency modulus	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.0	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Plasticity	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958	201	232	259	241	218	245	267	281	244	258	288	324	267	227	243	267	276	294	371	371
Compression	232	244	260	264	254	261	277	301	273	298	354	283	260	269	280	280	303	307	414	414
Recovery	96.9	96.0	94.5	89.7	96.2	94.6	90.7	81.4	95.9	93.0	87.7	70.3	293	273	269	269	269	269	269	269
Torsional resilience	37	41	53	83	38	58	76	174	43	66	98	234	—	—	—	45	57	67	89	115
Wt.958																				

TABLE 8—Continued  
NATURAL RUBBER

	Kosmos-T										Kosmos-F.4										Shawinigan										
Volume loading	31	10	15	20	25	30	50	10	15	20	25	34	10	15	20	25	34	10	15	20	25	34	10	15	20	25	34	10	15	20	25
Tensile strength	162	210	254	247	254	249	192	131	145	145	175	193	233	237	237	237	193	233	237	237	237	193	233	237	237	193	233	237	237	237	237
Elongation	705	641	605	584	530	476	244	612	622	631	637	673	603	532	489	439	673	603	532	489	439	673	603	532	489	439	673	603	532	489	439
Stress strain	9	14	20	18	27	36	79	13	18	12	17	10	18	27	26	26	10	18	27	26	26	10	18	27	26	10	18	27	26	26	
100%	14	23	37	40	59	78	157	19	25	20	25	18	35	56	66	87	18	35	56	66	87	18	35	56	66	18	35	56	66	87	
300%	19	39	68	79	105	133	—	30	38	35	43	28	60	95	115	143	28	60	95	115	143	28	60	95	115	28	60	95	115	143	
400%	30	70	114	128	167	201	—	49	59	59	71	44	100	149	167	195	44	100	149	167	195	44	100	149	167	44	100	149	167	195	
500%	53	115	167	194	227	—	—	80	92	91	111	78	159	216	—	—	78	159	216	—	—	78	159	216	—	78	159	216	—	—	
600%	95	177	251	—	—	—	—	102	137	—	—	138	208	—	—	—	138	208	—	—	—	138	208	—	—	—	138	208	—	—	
Shore hardness	37	43	53	60	65	70	85	47	56	60	66	42	49	57	63	68	42	49	57	63	68	42	49	57	63	42	49	57	63	68	
R.A.B.R.M. hardness	31	105	81	67	52	39	28	88	69	58	43	116	89	75	60	51	116	89	75	60	51	116	89	75	60	116	89	75	60	51	
S.E.	—	95	92	84	76	53	36	77	67	65	53	96	94	75	69	69	96	94	75	69	69	96	94	75	69	96	94	75	69	69	
Resilience 50° C	81.9	75.3	70.4	63.8	59.4	53.6	Too hard to test	57.4	47.2	40.8	33.9	84.1	78.9	74.8	69.7	63.6	84.1	78.9	74.8	69.7	63.6	84.1	78.9	74.8	69.7	84.1	78.9	74.8	69.7	63.6	
Indentation	15.8	14.4	13.1	12.0	11.1	9.8	—	13.9	12.0	11.7	10.6	14.6	13.4	12.2	11.2	10.4	14.6	13.4	12.2	11.2	10.4	14.6	13.4	12.2	11.2	14.6	13.4	12.2	11.2	10.4	
Permanent set 300° C	2	2	7	9	15	13	—	5	13	16	20	1	6	11	14	20	1	6	11	14	20	1	6	11	14	20	1	6	11	14	20
du Pont abrasion	419	321	234	205	167	153	172	401	315	246	191	301	243	207	167	156	301	243	207	167	156	301	243	207	167	301	243	207	167	156	156
Dunlop abrasion	—	—	—	—	—	—	—	—	Rolls	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Benzene swelling 25° C	—	.225	.140	.073	—	.148	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	.222	.195	.095	—
2 days	380	340	291	255	228	209	163	402	398	392	389	343	289	257	232	212	343	289	257	232	212	343	289	257	232	343	289	257	232	212	
Distention (° C) 1,000 revs.	75	96	105	116	119	130	133	190	172	192	177	66	78	82	81	84	66	78	82	81	84	66	78	82	81	66	78	82	81	84	
25 kg.	101	148	185	201	165	165	Ball bursts	65.1	56.6	50.7	54.4	96	126	140	144	164	96	126	140	144	164	96	126	140	144	96	126	140	144	164	
50 kg.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Dynamic resilience	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dynamic modulus	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
High frequency modulus	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Wt.0	—	48	80	148	247	—	—	383	106	231	380	—	62	84	134	200	—	62	84	134	200	—	62	84	134	—	62	84	134	200	
Wt.958	—	44	71	135	201	—	—	306	93	198	271	—	56	72	117	177	—	56	72	117	177	—	56	72	117	—	56	72	117	177	
Plasticity Compression	252	226	298	329	371	487	—	832	325	493	618	303	276	337	352	372	303	276	337	352	372	303	276	337	352	303	276	337	352	372	
Recovery	271	279	373	399	426	549	999	371	573	713	864	327	327	411	419	411	327	327	411	419	411	327	327	411	419	327	327	411	419	411	
Torsional resilience	95.8	91.4	87.7	82.4	79.4	73.5	63.3	77.6	68.5	64.5	62.1	96.6	92.7	89.6	82.9	74.3	96.6	92.7	89.6	82.9	74.3	96.6	92.7	89.6	82.9	96.6	92.7	89.6	82.9	74.3	

TABLE 9  
NEOPRENE-GN

Volumes Parts	Blank	Kosmos-T							
		10 15	15 22.5	20 30	25 37.4	30 45	40 60	50 74.8	
Tensile strength	162	233	232	231	237	224	219		
Elongation	854	777	761	576	542	430	290	201	
Modulus									
100%	11	17	20	27	32	45	76	107	
200%	15	53	44	59	76	100	167	—	
300%	20	58	80	105	124	166	—	—	
400%	27	89	120	149	180	—	—	—	
500%	41	125	160	—	—	—	—	—	
Hardness									
B.S.I.	121	86	76	61	48	43	28	20	
Shore	45	55	61	66	71	71	81	86	
Resilience									
25° C	71.9	69.1	65.5	62.4	57.4	56.1	42.8	37.2	
50° C	74.5	73.8	72.0	68.3	65.2	61.3	55.1	49.4	
100° C	73.4	72.3	71.7	67.6	65.2	64.6	57.1	53.2	
Abrasion									
du Pont	371	206	175	154	136	112	55	45	
Dunlop	—	—	.131	.074	.042	.041	.046	.068	
Swelling									
DTD.44D	41	36	30	29	29	26	23	19	
Benzene	461	331	374	273	201	215	189	163	
A.T.87F	187	107	91	85	94	82	74	66	
Plasticity									
Compression	110	121	140	173	325	254	431	533	
Recovery	32	38	37	33	48	78	146	150	
H. F. modulus									
0 g.	51	88	101	138	215	250	—	—	
958 g.	49	75	110	118	188	293	—	—	
Permanent set	9.4	5.1	4.5	2.4	1.1	1.9	2.3	2.8	
50 kg.									
75% Eb.	10.4	12.5	19.0	15.6	14.0	11.8	B	B	
Compression set	49	45	50	47	51	46	47	45	
Compression set	—	29	22	20	20	23	—	—	
(overcure)									
Tear									
20-25° C	49	91	79	100	103	113	66	63	
60-80° C	6	16	7	66	81	57	39	38	
Detrition (° C)	143	141	132	108	81	56	—	—	

Volumes Parts	Kosmos-40							Kosmos-20				
	10 15	15 22.5	20 30	30 45	40 60	50 74.8		15 22.3	30 44.4	45 66.8	60 88.9	75 111
Tensile strength	203	189	210	210	196	180	200	173	188	161	119	
Elongation	727	621	535	536	243	186	694	518	303	198	68	
Modulus												
100%	16	20	26	43	60	108	19	30	53	92	—	
200%	30	48	57	105	160	—	39	72	130	—	—	
300%	52	80	106	178	—	—	69	122	—	—	—	
400%	84	122	155	—	—	—	103	158	—	—	—	
500%	120	164	—	—	—	—	137	—	—	—	—	
Hardness												
B.S.I.	93	81	69	52	38	30	85	59	46	37	21	
Shore	53	60	64	68	79	81	56	68	75	83	88	
Resilience												
25° C	69.7	68.5	63.0	62.1	51.6	46.0	68.2	58.7	55.9	52.2	43.5	
50° C	74.5	72.4	71.0	66.3	61.3	58.5	74.1	68.1	63.9	61.3	53.2	
100° C	72.2	70.8	69.6	68.3	62.5	61.7	71.0	67.0	64.3	63.4	57.9	
Abrasion												
du Pont	221	166	164	113	82	32	228	196	128	97	64	
Dunlop	—	.163	.068	.044	.042	.047	—	.069	.068	.067	—	
Swelling												
DTD.44D	34	31	30	27	27	21	31	26	25	26	17	
Benzene	341	244	258	221	196	157	316	202	196	159	130	
A.T.87F	107	95	89	83	72	66	97	84	71	64	57	
Plasticity												
Compression	111	124	147	201	230	506	114	143	199	304	534	
Recovery	35	43	27	54	30	120	36	37	31	21	159	
H. F. modulus												
0 g.	79	98	122	182	280	—	88	146	242	360	580	
958 g.	79	116	109	158	292	—	95	142	288	300	515	
Permanent set	5.6	5.0	4.3	1.5	1.1	3.2	5.1	5.0	2.1	1.1	1.1	
50 kg.												
75% Eb.	11.3	13.6	12.6	8.5	3.9	4.3	12.9	11.6	B	B	B	
Compression set	50	48	49	47	45	48	49	48	50	51	56	
Compression set	27	27	24	24	22	—	28	26	23	23	20	
(overcure)												
Tear												
20-25° C	70	63	92	87	72	46	83	67	87	69	64	
60-80° C	12	9	54	37	31	24	23	11	35	25	24	
Detrition (° C)	138	130	99	—	56	—	135	116	69	73	—	

B = Ring broke during test.

TABLE 9—Continued  
NEOPRENE-GN

	Magecol					Thermax					
Volumes Parts	15	30	45	60	75	20	40	60	80	100	120
	22.3	44.4	66.8	88.9	111	29.7	59.5	88.9	118.9	138.4	177.8
Tensile strength	161	151	165	151	128	161	146	148	144	134	127
Elongation	695	441	269	162	70	712	500	367	250	188	127
Modulus											
100%	20	48	77	110	—	18	30	41	68	92	117
200%	41	94	143	—	—	—	—	—	—	—	—
300%	69	128	—	—	—	51	100	136	—	—	—
400%	96	—	—	—	—	—	—	—	—	—	—
500%	—	—	—	—	—	114	—	—	—	—	—
Hardness											
B.S.I.	80	51	38	31	22	90	69	53	40	31	25
Shore	59	71	80	82	89	51	59	65	74	81	86
Resilience											
25° C	68.1	60.7	56.3	51.3	46.3	70.9	68.7	57.5	54.8	50.6	60.7
50° C	72.8	68.7	64.0	60.7	52.9	65.8	73.2	64.6	64.8	60.0	54.8
100° C	71.1	68.5	63.4	62.1	58.8	71.0	69.1	65.1	62.1	59.4	57.1
Abrasion du Pont	249	219	186	155	114	341	340	283	267	215	148
Dunlop	—	—	.138	.136	.145	—	.234	.208	.165	.159	.221
Swelling											
DTD.44D	33	26	23	22	17	34	28	26	22	19	17
Benzene	300	218	169	147	115	324	240	218	166	139	117
A.T.87F	98	78	67	60	52	105	94	78	71	56	51
Plasticity											
Compression	113	150	200	299	557	130	142	148	187	207	265
Recovery	36	35	27	16	123	26	18	23	17	26	123
H. F. modulus											
0 g.	95	178	269	436	531	72	—	153	—	364	—
958 g.	93	157	292	416	448	76	—	157	—	296	—
Permanent set	3.0	3.9	2.2	2.3	B	4.1	8.4	1.7	1.1	1.1	1.2
50 kg.											
75% Eb.	16.4	11.8	11.5	2.3	B	12.4	10.3	8.3	8.4	2.5	B
Compression set	52	50	48	51	39	50	49	53	57	51	48
Compression set (overcure)	24	17	15	15	15	25	29	23	27	24	—
Tear											
20-25° C	57	57	72	52	66	65	84	76	—	49	45
60-80° C	14	13	32	21	28	23	21	24	—	24	27
Detrition ° C	125	104	67	66	—	77	—	—	—	—	—

B = Ring broke during test.

The choice of black obviously depends on the various requirements needed for service, but in any case the same choice does not necessarily hold over the whole hardness range.

With the exception of tires, the usual properties demanded are ease of processing, good resilience, coupled with reasonable tensile strength, while oil resistance requires the use of the largest amounts of filler possible.

In Neoprene-GN the blacks tested appear to fall into two resilience groups, although it should be noted that the resilience variation between the black loadings which give an equivalent hardness is quite small.

Group (1) Kosmos-T, Kosmos-40 and Kosmos-20.

Group (2) Magecol, Thermax.

On purely economic grounds it would always be desirable to use Thermax as larger amounts of filler could be used, but consideration of the resultant physical properties such as abrasion or tear require other choices to be made. In the very hard range, i.e., above 85° Shore, it is obvious that to retain reasonable elongation properties, it would be necessary to use a channel black of the Kosmos-T type, or a mixture of Kosmos-T and Thermax or Magecol. A mixture may be more desirable for processing, although the addition of large quantities of channel blacks to Neoprene is easier than with natural rubber.

In general, the choice of carbon black for Neoprene-GN is not critical, since

the variation obtained with some properties over the present range of carbon blacks is small. The following table gives the ratio of one black to another relative to a given hardness.

B.S. Hardness	30		50		75	
	Natural rubber	Neoprene-GN	Natural rubber	Neoprene-GN	Natural rubber	Neoprene-GN
Kosmos-T	—	1.00	1.00	1.00	1.00	1.00
Kosmos-40	—	1.17	—	1.24	—	1.28
Kosmos-20 or S.B.I.	—	1.37	1.62	1.58	1.42	1.70
Magecol	—	1.14	1.50	1.23	1.42	1.54
Thermax	—	2.27	2.52	2.56	2.52	2.59

### CONCLUSIONS

1. All the blacks tested can be incorporated into Neoprene-GN much more easily than into natural rubber, and the limits of loading are higher with Neoprene-GN than with natural rubber.

2. A broader maximum in the tensile strength-volume loading curve is obtained with Neoprene-GN, and it has been found that the two coarse blacks do not reinforce Neoprene-GN.

3. Tables show the grading of each carbon black with each physical property. It has been found that, in general, the results correlate with measurements of particle size and surface area.

4. Even so, if dynamic conditions are met in service, it is necessary to evaluate the degree of reinforcement under dynamic conditions.

5. With natural rubber, each black tends to have its own correlation between dynamic and static hardness tests, whereas with Neoprene-GN one correlation exists for all blacks.

6. Within a given polymer it is sufficient to do only compression plasticity (Williams) measurements, and recovery measurements are required only when comparing different polymers.

7. Measurements of tear resistance with Neoprene-GN have shown that, as the particle size of the blacks decreases, the peakiness of the tear resistance volume loading curve is increased, particularly at higher temperatures.

8. Torsional resilience and impact resilience have a very high correlation in natural rubber.

9. Different carbon blacks in Neoprene-GN produce very small changes in resilience.

10. With increased loadings of black the resilience properties of both rubbers become more sensitive to temperature.

11. On both the du Pont and Dunlop abrasion machines, there is fairly good agreement between abrasion resistance and particle size.

12. With natural rubber, if the hardness is maintained constant and resilience increased, the heat build-up decreases, whereas with Neoprene-GN under the same conditions the heat build-up increases.

13. When comparing compounds of different hardness for heat build-up, a constant deformation test is preferable to a constant load test.

14. There is a good correlation between swelling in benzene and modulus measurements. The correlation is better with Neoprene-GN than with natural rubber.



## APPENDIX

As the results given in this paper refer specifically to certain tests, it is important that the methods of testing be referred to in certain cases. Details of the more important tests as carried out in the I.C.I. Rubber Service laboratories during the period covered by this paper are given below.

1. *Tensile strength, elongation at break and stress strain.*—Six rings were cut from a 4 mm. sheet. The natural rubber was cut on a Schopper cutter and the Neoprene-GN on a Goodbrand rotary cutter. In all cases the six rings were tested on the modified Schopper testing machine at the normal speed of separation of 40 cm. per min. The modification referred to is the inclusion of a drive to rotate the top pulley.

2. *Shore hardness.*—In all cases tests were carried out on sheets 4 mm. thick at the laboratory temperature with a Shore durometer. The natural rubber results were obtained before the durometer was calibrated properly<sup>10</sup>, but the Neoprene-GN results were obtained using a standardized Shore durometer operated on a stand.

3. *B.S. hardness.*—In all cases tests were carried out at the laboratory temperature on two superimposed discs of total thickness 8–9 mm., using a method complying with the British Standards Institution Specification BS.903, 1940.

4. *Resilience (tripsometer).*—Strips of material (8 × 8 × 4 mm.) were cut and buffed on one side to a thickness of 4 mm. ± 0.1 mm. These were tested on the Dunlop tripsometer at controlled temperatures, using a 45° angle of fall.

5. *High-frequency modulus and resilience.*—Circles (38 mm. diameter, 19 mm. thick) were moulded and tested under two conditions of test, (1) static load 0 g., (2) static load 958 g.<sup>16</sup>

6. *Plasticity.*—Three 2-cc. pellets were cut from the unvulcanized compounded stock and tested in the Williams plastomer at 82.5° C under a 5-kg. load. The compression reading was taken after the load had been applied for 3 minutes. At the end of this period the load was released, the sample removed from the oven, allowed to recover for 1 minute, and the height measured.

7. *Tear resistance.*—This test was carried out according to A.S.T.M. D.624–44 T.

8. *Compression set.*—This test was carried out according to A.S.T.M. D.395–40 T, Method B. Samples 25 mm. diameter and 9.5 mm. thick were compressed by 30 per cent for 22 hours at 70° C and the thickness remeasured after resting 30 minutes at room temperature.

9. *Swelling.*—Samples 20 mm. square by 4 mm. thick were used for benzene swelling tests. The volume increase was measured according to A.S.T.M. D.471–44 T.

10. *du Pont abrasion.*—The test was carried out according to A.S.T.M. 394–40 T.

11. *Dunlop abrasion.*—The test was carried out on a controllable slip abrasion machine referred to by Parkinson<sup>4</sup>, using a 16 per cent slip.

12. *Torsional resilience.*—This test has been designed in the I.C.I. Rubber Service Laboratories and is not described in the literature. Moulded dumbbells are used. The sample can be held under varying degrees of extension, and by means of a mirror mounted in the center of the narrow portion of the dumbbell, successive amplitudes of the deflection are noted.

13. *Dynamic resilience.*—This test has been designed by the I.C.I. Rubber Service Laboratories and has been described by Naunton and Waring<sup>16</sup>.

Circles (38 mm. diameter, 19 mm. thick) are precompressed between two rigid plates. Between the two samples, a pendulum is held, which may be deflected, putting the rubber under an angular compressive strain. The pendulum is released and the successive damping curves are recorded. The stress cycle of the system is of the order of about one-half second or less.

## ACKNOWLEDGMENT

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# ALKALINE MATERIALS AS ACCELERATORS FOR GR-S \*

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During the development of the national synthetic rubber program it was decided to utilize the research and development facilities of compounding material suppliers in an investigation to determine the best methods of formulating GR-S and other synthetic rubbers.

This investigation was directed by the Compounding Research Branch of the Office of the Rubber Director, which then collected and distributed to the participating laboratories the large amount of data gained from the many tests carried on with different accelerators, fillers, and softeners in GR-S. Included in this information were indications that the curing rate of GR-S was affected to a considerable degree by inorganic oxides and alkaline materials. Consequently this phase of the problem was investigated still further in this laboratory, and some data were released through the same agency regarding the efficacy of magnesia, litharge, and red lead as activators for some organic accelerators.

The results obtained encouraged further work to determine the effect of more strongly alkaline materials. It was discovered that ethanolamines were very effective activators for some organic accelerators; in fact, triethanolamine activates tetramethylthiuram monosulfide so strongly that a combination of the two materials promotes vulcanization of GR-S at room temperature.

## ORGANIC BASES AS PRIMARY ACCELERATORS

Since these organic bases proved to be powerful secondary accelerators, the investigation was extended to determine the value of these and other basic materials as primary accelerators. Magnesia and litharge alone are weak accelerators for GR-S, but various amines and sodium hydroxide proved themselves to be very active. Certain combinations of magnesia and of sodium hydroxide with organic bases were found to be even more powerful, and even amides and inorganic ammonium salts exhibited considerable accelerating strength in the presence of magnesia. Furthermore, zinc oxide was not required to develop the full strength of these agents.

Such combinations not only affect the rate of vulcanization of GR-S, but they also produce vulcanizates with excellent physical properties, which in some respects are superior to those developed by normal acceleration.

Of considerable significance, also, is the fact that the cost of many of these combinations is lower than that of the more common organic accelerators required to produce an equivalent rate and state of vulcanization of GR-S.

## EXPERIMENTAL DETAILS

An indication of the accelerating activity of combinations of magnesia and organic bases was obtained first in a series of experiments with GR-S stocks

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TABLE 1  
WHITE GR-S STOCKS WITH TRIETHANOLAMINE AND MAGNESIA

Compound	A	B	C*	D
GR-S	100.0	100.0	100.0	100.0
Titanium dioxide	25.0	25.0	25.0	25.0
Zinc oxide	2.0	2.0	2.0	2.0
Turqum	5.0	5.0	5.0	5.0
Magnesia	10.0	..	5.0	4.0
Triethanolamine	..	5.0	2.5	1.5
Sulfur	4.0	4.0	4.0	4.0

\* Compound C was a blend of A and B

#### PHYSICAL PROPERTIES

Compound	Original				After air oven aging 136 hrs. at 100° C		
	Cure at 287° F (mins.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)
A	30	625	1000	125	1090	650	295
B	30	260	1150	65	710	575	260
C	30	1080	625	310	1350	510	685
D	15	1275	885	185	1320	510	515
D	30	1750	665	335	1660	480	650

TABLE 2  
BLACK GR-S STOCKS WITH TRIETHANOLAMINE AND MAGNESIA

Compound	A	B	C	D	E	F
GR-S	100.0	100.0	100.0	100.0	100.0	100.0
HMF black	20.0	20.0	20.0	20.0	20.0	20.0
Zinc oxide	..	..	..	..	2.0	..
Magnesia	5.0	..	1.0	2.0	..	2.0
Triethanolamine	..	1.0	1.0	1.0	1.0	2.0
Sulfur	3.0	3.0	3.0	3.0	3.0	2.0

#### PHYSICAL PROPERTIES

Compound	Original				After air oven aging at 100° C—4 days		
	Cure at 287° F (mins.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)
A	15	65	1300	..	..	..	..
A	30	250	1150	..	..	..	..
B	15	695	1025	100	1100	525	385
B	30	1100	735	200	1245	395	740
B	45	1215	625	295	1090	330	910
C	15	905	900	165	2115	600	625
C	30	1730	710	365	2070	460	990
C	45	1910	610	475	2190	440	1155
D	15	1190	875	190	2410	600	790
D	30	1750	635	410	2030	420	1150
D	45	1875	550	590	2315	400	1475
E	30	80	1425	25	..	..	..
E	45	210	1375	55	..	..	..
F	15	1540	725	345	2080	540	875*
F	30	2110	635	545	2340	540	975*
F	45	2360	620	640	2430	535	1025*

\* Aged 89 hours

TABLE 3  
MAGNESIA AND VARIOUS AMINES AS ACCELERATORS FOR GR-S

Compound	A	B	C	D	E
GR-S	100.0	100.0	100.0	100.0	100.0
HMF black	20.0	20.0	20.0	20.0	20.0
Magnesia	2.0	2.0	2.0	2.0	2.0
Monoethanolamine	0.4	..	..	..	..
Diethanolamine	..	0.7	..	..	..
Triethanolamine	..	..	1.0	..	..
Tetraethanolamine ammonium hydroxide (40%)	..	..	..	3.5	..
Tetraethylene pentamine	..	..	..	..	0.25
Sulfur	3.0	3.0	3.0	3.0	3.0

PHYSICAL PROPERTIES

Compound	Original				After air oven aging at 100° C—4 days		
	Cure at 287° F (mins.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)
A	15	570	1060	110	1975	750	410
A	30	1235	835	210	2150	585	670
A	45	1775	750	295	2255	505	945
B	15	980	925	160	2260	590	665
B	30	1645	725	305	2050	530	1030
B	45	2080	640	465	1770	350	1525
C	15	1190	875	190	2410	800	790
C	30	1750	635	410	2030	420	1150
C	45	1875	550	590	2515	400	1475
D	15	1720	755	305	2600	520	1030
D	30	1850	545	585	2150	410	1300
D	45	1800	480	735	1975	365	1455
E	15	1900	775	320	1730	400	1125
E	30	2000	540	670	1880	375	1360
E	45	1730	450	820	1550	315	1445

TABLE 4  
AMINES ALONE AS ACCELERATORS

Compound	A	B	C	D
GR-S	100.0	100.0	100.0	100.0
HMF black	20.0	20.0	20.0	20.0
Monoethanolamine	0.8	..	..	..
Ethylene diamine (70%)	..	0.57	..	..
Triethylene tetramine	..	..	0.47	..
Tetraethylene pentamine	..	..	..	0.5
Sulfur	3.0	3.0	3.0	3.0

PHYSICAL PROPERTIES

Compound	Original				After air oven aging at 100° C—4 days		
	Cure at 287° F (mins.)	Tensile strength (lbs. per sq. in.)	Elonga- tion (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elonga- tion (%)	Modulus at 300% (lbs. per sq. in.)
A	15	1115	815	175	1025	365	690
A	30	1590	550	385	1025	275	..
B	15	1020	960	115	930	390	555
B	30	1380	685	255	880	290	820
C	15	1365	775	205	1010	360	945
C	30	1505	560	460	1340	310	1280
D	15	1350	750	235	1335	370	925
D	30	1580	560	475	1145	265	..

TABLE 5  
AMINE AND MAGNESIA IN GR-S

Compound	A	B	C	D	E
GR-S	100.0	100.0	100.0	100.0	100.0
HMF black	20.0	20.0	20.0	20.0	20.0
Magnesia	..	..	..	2.0	2.0
Tetraethylene pentamine	0.5	1.0	3.0	0.5	1.0
Sulfur	2.0	2.0	2.0	2.0	2.0

PHYSICAL PROPERTIES

Compound	Original				After air oven aging at 100° C—4 days		
	Cure at 287° F (mins.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)
A	10	710	915	135	920	385	580
A	15	1125	825	205	925	335	720
A	20	1415	770	245	900	310	835
A	30	1600	640	400	810	265	..
B	10	1500	860	210	740	275	..
B	15	1805	745	350	670	230	..
B	20	1825	665	415	645	220	..
B	30	1880	615	500	590	195	..
C	10	1705	900	205	1150	390	790
C	15	1810	750	280	1100	350	850
C	20	1820	660	380	1000	330	875
C	30	1665	645	425	720	250	..
D	10	1535	785	290	1800	385	1080
D	15	1635	665	450	1545	345	1255
D	20	1710	510	530	1280	280	..
D	30	1960	525	735	1300	285	..
E	10	2000	745	415	1975	425	1100
E	15	2310	640	535	1710	350	1295
E	20	2285	590	670	1910	355	1430

TABLE 6  
SODIUM HYDROXIDE AND MONOETHANOLAMINE IN GR-S

Compound	A	B	C	D
GR-S	100.0	100.0	100.0	100.0
HMF black	20.0	20.0	20.0	20.0
Sodium hydroxide	1.5	..	..	1.0
Monoethanolamine	..	1.0	1.5	0.5
Sulfur	3.0	3.0	3.0	3.0

PHYSICAL PROPERTIES

Compound	Original				After air oven aging at 100° C—4 days		
	Cure at 287° F (mins.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)
A	15	1015	775	160	1670	480	690
A	30	1520	630	320	1715	410	990
B	15	1100	755	200	1000	380	670
B	30	1350	535	445	1100	275	..
C	15	1520	715	280	1220	350	915
C	20	1520	605	405	1165	300	1165
C	30	1465	515	555	1025	245	..
D	15	1475	690	300	1595	420	880
D	20	1550	615	370	1715	390	1050
D	30	1810	560	530	1520	325	1335



containing no carbon black. In these tests (Table 1) white GR-S compounds accelerated only with magnesia (A) and triethanolamine (B) were soft, weak, and definitely undercured; whereas stocks containing both of these materials were well cured and snappy (C and D).

Additional tests with black stocks (Table 2), with smaller amounts of magnesia and triethanolamine, show that magnesia alone (A) has little value as an accelerator for GR-S, but that triethanolamine by itself is fairly active (B). The activity of triethanolamine is increased considerably by the presence of magnesia (C and D), but is retarded by zinc oxide (E). It will be noticed also that after aging, the physical properties of C and D are considerably better than B. Compound F demonstrates still further the activity and good aging characteristics of these combinations.

Combinations of magnesia with primary, secondary, and tertiary amines, quaternary ammonium bases, and polyethylenamines are also very active accelerators for GR-S, as can be seen from the data in Table 3. The comparison of these amines in GR-S was made on an equivalent weight basis, i.e., the

TABLE 7

ORGANIC AND INORGANIC BASE *vs.* NORMAL ACCELERATION FOR GR-S

Compound	A	B	C
GR-S	100.0	100.0	100.0
EPC black	20.0	20.0	20.0
HMF black	20.0	20.0	20.0
Paraflux	5.0	5.0	5.0
Zinc oxide	3.0	..	..
Santocure	1.2	..	..
Monoethanolamine	..	2.0	1.5
Magnesia	..	2.0	..
Sodium hydroxide	..	..	1.5
Sulfur	2.0	3.0	3.0

## PHYSICAL PROPERTIES

Compound	Original				After air oven aging at 100° C					
					24 Hours			4 Days		
	Cure at 287° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)
A	20	2220	850	375	1565	250	..	1885	225	..
A	30	2890	675	730	1930	290	..	1955	220	..
A	45	2690	575	915	1820	305	1780	1610	220	..
A	60	2620	545	1000	1575	285	..	1770	240	..
B	20	2800	675	705	3050	575	1200	2980	445	..
B	30	3130	620	905	2925	490	1450	2900	410	1980
B	45	2880	545	1085	2750	445	1570	2760	375	2100
B	60	2900	515	1210	2800	440	1670	2715	375	2180
C	20	2680	635	675	2780	515	1270	2610	400	1840
C	30	3040	600	935	2700	455	1500	2460	360	2000
C	45	2800	545	1020	2700	440	1590	2450	350	2040
C	60	2900	530	1100	2250	375	1720	2375	335	2100
Hot bend flexing at 100° C										
Flex Cycles		350	500	750	1000	2000	3000	4000	8700	10000
A 60 min.	Crack width (inches)	0.15	0.20	0.35	0.40	0.75	0.85	1.00*	..	..
B 60 min.		0.05	0.05	0.05	0.10	0.20	0.30	0.40	0.85	0.85
C 60 min.		0.05	0.05	0.10	0.15	0.35	0.40	0.50	0.70	0.70

\* Sample cracked entire through.

Note: These samples were flexed according to ASTM Method D 13-44T with the exception that the hole in the sample penetrated to about 0.05 inch instead of completely piercing the sample, and the flexing was conducted at 400 instead of 300 cycles a minute.

molecular weight of the respective amines and the number of amine nitrogen atoms in each were used in determining the amounts used.

Monoethanolamine and polyethyleneamines were compared in compounds containing no magnesia (Table 4). Here the amine content was increased because of the absence of magnesia from these formulations. It will be noticed that, even under these conditions, all of these materials are active accelerators for GR-S.

However, according to the data in Table 5, a combination of magnesia and tetraethylene pentamine (D and E) will produce faster curing stocks with better physical properties, both before and after aging, than appear to be attainable with the amine alone.

TABLE 8  
VARYING BLACK CONTENT WITH BASIC ACCELERATION

Compound	A	B
GR-S	100.0	100.0
HMF black	15.0	12.5
Paraflex (asphalt)	5.0	5.0
Magnesia	2.0	1.5
Tetraethylene pentamine	0.5	0.375
Sulfur	3.0	3.0

#### PHYSICAL PROPERTIES

Compound	Original				After air oven aging at 100° C—4 days		
	Cure at 287° F (mins.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)
A	10	1800	690	380	1500	395	945
A	15	1845	560	570	1450	345	1130
A	20	1565	465	690	1440	335	1210
A	30	1370	400	825	1335	290	..
B	10	1640	815	250	1365	420	745
B	15	1460	615	350	1350	370	915
B	20	1535	570	435	1365	355	995
B	30	1445	495	550	1210	295	..

#### Heat build-up—Goodrich flexometer

	Min. cure	Temp. (F*)	Compression (%)			% Permanent set
			Static	Initial dyn.	Final dyn.	
A	45	66	19.2	8.9	8.9	3.6
B	45	72	21.8	11.6	11.6	5.0

\* Temp. F equals temperature rise in degrees Fahrenheit.

Note: Conditions of the test were: duration, 30 min.; load, 100 lbs. per sq. in.; stroke, 0.2 inch. Sample A was tested at 72° F and B at 76° F.

Experiments with sodium hydroxide show that it is an accelerator for GR-S and that a combination of this hydroxide with monoethanolamine is also very active. The results of this work are given in Table 6.

As stated earlier, combinations of organic bases with magnesia and with sodium hydroxide not only are active accelerators for GR-S, but they also produce vulcanizates with excellent physical properties. A comparison between GR-S treated stocks accelerated with some of these combinations and accelerated with Santocure (*N*-cyclohexyl-2-benzothiazyl sulfenamide) is given in Table 7.

Since the more lightly loaded a GR-S stock is, the less heat it will generate during flexing, some work was done to learn if it were possible to develop a low-black GR-S carcass stock with good physical properties by utilizing some of these accelerator combinations of organic and inorganic bases. The results of these tests are given in Table 8.

#### BUTADIENE-ACRYLONITRILE POLYMERS

The effectiveness of combinations of organic and inorganic bases as accelerators for butadiene-acrylonitrile copolymers was also investigated, and it was found that tetraethylene pentamine and magnesia are an active accelerator combination for Hycar-OR and Perbunan-26.

TABLE 9

#### AMINE AND MAGNESIA WITH NITRILE RUBBERS

Compound	A	B
Hycar OR-15	100.0	
Perbunan-26		100.0
HMF black	20.0	20.0
Bardol	20.0	15.0
Magnesia	2.0	2.0
Tetraethylene pentamine	0.5	0.5
Sulfur	2.0	2.0

#### PHYSICAL PROPERTIES

Compound	Original				After air oven aging at 100° C—4 days			
	Cure at 287° F (mins.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	
A	10	2500	750	450	2475	340	2125	
A	15	3195	650	670	2940	355	2240	
A	30	2420	490	960	3100	345	2480	
B	5	1645	775	265	1940	385	1250	
B	10	2170	575	570	2210	380	1375	

#### DISCUSSION

Many other products having strong basic properties also produce results similar to those recorded in this paper. Among these are long-chain aliphatic amines; the aromatic amine, benzylamine; and the closed ring aliphatic amines, piperidine and morpholine.

The weak bases, pyridine, aniline, and hexamethylenetetramine, exhibit little activity, even in the presence of magnesia. Various amides and salts of amines, such as urea, acetamide, and long-chain aliphatic amine acetates, are inactive when used alone, but are fairly active in the presence of magnesia.

Although GR-S stocks accelerated with some of these combinations did not vulcanize in several hours at 100° C, there is the possibility that many of them might be somewhat "scorchy" in regular production use.

Also, some of the amines may be somewhat toxic, and this factor should be evaluated before considering them for factory use.

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## STYRENE-DIENE RESINS IN RUBBER COMPOUNDING \*

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Early in the investigation of butadiene-styrene copolymers as synthetic rubbers, this laboratory became interested in copolymers containing much more styrene than any of the American or German synthetics. This interest was soon directed to the resinous copolymers obtained when the styrene content is increased beyond the range in which rubberlike properties are observed at room temperature.

The exploratory work, therefore, involved preparation and evaluation of butadiene-styrene copolymers containing from 65 to 98 per cent styrene. No description of similar polymers has been found. Konrad and Ludwig<sup>1</sup> claimed the improvement of rubberlike properties of butadiene-styrene copolymers by increasing the styrene content from the normal range to "between about 47.5 and about 70 per cent". The claims and examples of this patent emphasize the improvement of rubberlike properties, such as tensile, elongation, and rebound, at high temperatures. It is well known in this country, however, that increase in styrene content beyond a certain point, perhaps 50-55 per cent, is accompanied by a loss of overall balance of rubber characteristics. Therefore, the copolymers at the upper end of the range described by Konrad and Ludwig have definite limitations for rubber uses—for example, low rebound, high brittle point, shortness, etc.

In the writers' laboratory useful resins have been prepared from dienes and vinyl aryl hydrocarbons in the range 5 to 20 per cent diene and 80 to 95 per cent vinyl aryl hydrocarbon. This paper describes the properties and certain uses of one of these copolymers containing approximately 15 parts of butadiene and 85 parts of styrene. This material possesses a combination of physical and chemical properties which permit its use in several applications where cyclized natural or synthetic rubbers are commonly employed. Cyclized natural rubber has been described by Bruson<sup>2</sup>, Endres<sup>3</sup>, and Thies and Clifford<sup>4</sup>. Cyclized synthetic rubbers were described recently by Endres<sup>5</sup>. One product of this type is made from a special synthetic rubber.

The new 15 butadiene-85 styrene copolymer is now identified as Pliolite S-3, since it may be used in many Pliolite applications, often with distinct advantages over either the natural or synthetic rubber derivatives.

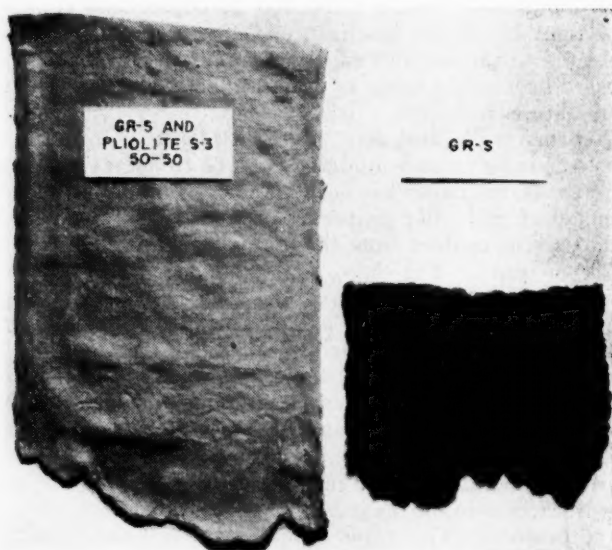
### PROPERTIES

Pliolite S-3 is a white thermoplastic crumb or powder with a heat distortion point of 40-45° C. It is practically odorless and is nontoxic in normal handling and processing. Only a small amount of nonhydrocarbon is present in the resin, including 0.5 per cent antioxidant. The resin has a specific gravity of approximately 1.05.

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Aliphatic solvents have only a moderate effect on this copolymer, but the resin is much less resistant to aromatics and chlorinated solvents. By hot milling it can be made soluble in such solvents as benzene, toluene, ethylene dichloride, and methyl ethyl ketone. Low-viscosity solutions of greater than 20 per cent solids can be made in these solvents.

Resistance of the resin to acids and alkalis is excellent. It is more resistant to oxidation than cyclized natural or synthetic rubbers. Prolonged exposure to air even at elevated temperatures does not cause appreciable change. Under severe conditions, solubility of the resin may decrease slightly, but no effect on the stiffening action of the resin in rubber compounds has been observed.



Comparison of Shrinkage and Smoothness of Equal Weights of GR-S (right) and of a 50-50 Blend of GR-S with Pliolite S-3 (left) Taken from a Cool Mill

The moisture absorption of Pliolite S-3 is very low. After 20 hours' immersion at 70° C, the molded resin absorbs only about 3.0 to 6.0 mg. of water per square inch of surface. The electrical properties of Pliolite S-3 are typical of those of hydrocarbon polymers. The following ranges of values have been obtained on testing at one kilocycle at 35° C:

Dielectric constant	2.5-2.6
Power factor (percentage)	0-0.02
Loss factor	0-0.004
Specific resistivity (ohm-cm.)	$0.8-1.6 \times 10^{14}$

Pliolite S-3 can be handled in an open mill, internal mixer, calender, or extruder, and can be molded readily. For Banbury mixing with GR-S, the usual procedure is to add GR-S first, then the 15 butadiene-85 styrene copolymer.

#### PROCESSABILITY AND COMPATIBILITY

Pliolite S-3 can be banded readily on a hot mill. A mill temperature of approximately 215° F is satisfactory. Rubber and various types of synthetic

rubber can then be added to the band. The addition must be rather slow at first, but the increments can be larger after the first additions have been well dispersed. If the first addition is not made slowly, the band shreds and causes difficulty in mixing. Among the synthetic rubbers which are mechanically compatible with Pliolite S-3 are GR-S, Neoprene, Chemigum N-1, Chemigum N-2, Chemigum N-3, Butyl, polyisoprene, butadiene-chlorostyrene, Vistanex, and polyethylene. Natural rubber is also compatible with the resin. The various synthetic rubbers and natural rubber can be admixed with Pliolite S-3 in any proportions. The 50-50 resin-rubber blends of 15 butadiene-85 styrene copolymer with GR-S, Butyl, butadiene-chlorostyrene, and polyisoprene are rather stiff and display white cracks when bent on a 180° angle. After cold remilling, these blends become smoother and more flexible.

The smoothness of GR-S and other synthetic rubbers during processing is improved by the presence of Pliolite S-3. Milled sheets, such as 50-50 GR-S-Pliolite S-3 have unusually low shrinkage when removed from the mill. To obtain particularly smooth processing stock for wire insulation, etc., the GR-S has been peptized to low Mooney viscosity before the blending operation. The reduced nerve of peptized GR-S allows Pliolite S-3-GR-S blends to extrude smoothly even in the absence of any compound loading.

### COMPOUNDING

For natural rubber and the various synthetic rubbers the 15-85 copolymer behaves as a stiffening agent somewhat similarly to the way shellac or Pliolite was used before the start of World War II. As little as 5 or 10 parts gives some stiffness to GR-S compounds. This amount can be increased as much as desired, with an attendant increase in stiffness and hardness. Compounds containing as high as 50 parts of the resin per 100 parts of GR-S appear quite rubberlike after curling and retain considerable resilience. Ordinary fillers and softeners may be used in Pliolite S-3 blends with rubber and synthetic rubbers. No distortion during cure is caused by the presence of the 15-85 copolymer in synthetic rubber stocks, and articles may be removed from hot molds in the normal manner without change in size or shape.

The rate of vulcanization of GR-S is not retarded by the presence of Pliolite S-3. Normal sulfur and accelerator ratios such as are required for GR-S are satisfactory for Pliolite S-3 blends with GR-S. The resin itself can be vulcanized in the following recipe: Pliolite S-3, 100 parts by weight; zinc oxide, 5; stearic acid, 0.5; sulfur, 2.5; Santocure, 1.5; total, 109.5 parts. The Shore hardness of the vulcanizate (D-scale) is 70-80; the Rockwell hardness (M-scale) is 70-75. Heat distortion and benzene solubility data follow:

	Heat distortion point (° C)	Solubility in benzene (%)
Uncured	..	100
Cured 5 min. at 320° F	43	23.5
Cured 10 min. at 320° F	..	6
Cured 20 min. at 320° F	47	3
Cured 30 min. at 320° F	53	..

In mill mixing it is advisable to introduce the sulfur and accelerator last, at a mill temperature as low as permits the particular stock to stay smooth. This procedure tends to prevent scorching.



TABLE I  
HARDNESS OF Pliolite S-3 BLENDS WITH GR-S AND CREPE RUBBER

Resin-rubber ratio	Shore hardness		Rockwell, M-scale
	A-scale	D-scale	
10 Pliolite S-3-90 GR-S	35	..	..
30 Pliolite S-3-70 GR-S	39	..	..
50 Pliolite S-3-50 GR-S	72	13	..
70 Pliolite S-3-30 GR-S	> 100	55	..
90 Pliolite S-3-10 GR-S	> 100	75	45
100 Pliolite S-3	> 100	..	68
10 Pliolite S-3-90 pale crepe	28	6	..
30 Pliolite S-3-70 pale crepe	55	12	..
50 Pliolite S-3-50 pale crepe	75	22	..
70 Pliolite S-3-30 pale crepe	75	32	..
90 Pliolite S-3-10 pale crepe	100	75	43
100 Pliolite S-3	> 100	..	68
10 Pliolite-90 GR-S	25	5	..
30 Pliolite-70 GR-S	36	6	..
50 Pliolite-30 GR-S	75	13	..
70 Pliolite-30 GR-S	90	35	..
90 Pliolite-10 GR-S	> 100	70	52
100 Pliolite	> 100	80	72
10 Pliolite-90 pale crepe	22	..	..
30 Pliolite-70 pale crepe	45	5	..
50 Pliolite-50 pale crepe	75	18	..
70 Pliolite-30 pale crepe	100	45	..
90 Pliolite-10 pale crepe	> 100	75	45
100 Pliolite	> 100	80	72

TABLE II  
TENSILE STRENGTH AND STIFFNESS OF Pliolite S-3  
BLENDS WITH GR-S AND CREPE RUBBER

Resin-rubber ratio	Tensile strength (lb. per sq. in.)	Elongation (%)	Relative torsion modulus	Olsen stiffness (inch-lb.)
10 Pliolite S-3-90 GR-S	60	925	0.023	0.016
30 Pliolite S-3-70 GR-S	60	385	0.023	0.021
50 Pliolite S-3-50 GR-S	550	70	0.50	0.215
70 Pliolite S-3-30 GR-S	1900	20	22	0.90
90 Pliolite S-3-10 GR-S	4350	5	44	2.41
10 Pliolite S-3-90 pale crepe	75	780	0.023	0.023
30 Pliolite S-3-70 pale crepe	300	420	0.233	0.058
50 Pliolite S-3-50 pale crepe	530	180	0.73	0.205
70 Pliolite S-3-30 pale crepe	1590	50	8.0	0.61
90 Pliolite S-3-10 pale crepe	3700	3	89.0	2.61
10 Pliolite-90 GR-S	50	550	0.023	0.015
30 Pliolite-70 GR-S	75	290	0.023	0.018
50 Pliolite-50 GR-S	320	60	1.09	0.25
70 Pliolite-30 GR-S	800	0	89.0	Broke
90 Pliolite-10 GR-S	2310	0	89.0	Broke
10 Pliolite-90 pale crepe	..	..	0.023	0.019
30 Pliolite-70 pale crepe	190	525	0.023	0.012
50 Pliolite-50 pale crepe	810	235	0.50	0.143
70 Pliolite-30 pale crepe	2350	15	89.0	0.75
90 Pliolite-10 pale crepe	3860	3	29.0	Broke

## BLENDS WITH GR-S AND CREPE RUBBER

The data in Table I indicate the degree of stiffening caused in GR-S and crepe rubber by the addition of increment amounts of Pliolite S-3 and of ordinary Pliolite, which is cyclized rubber. Both of the resins behave similarly in increasing the hardness of uncured stocks.

Table II shows that the increase in tensile strength and stiffness with increase in resin content is accompanied by a loss of extensibility. Over the range of composition shown, uncured blends of Pliolite S-3 with GR-S have higher tensile strengths, higher elongations but lower stiffness values than the corresponding blends of natural rubber Pliolite with GR-S. In uncured blends with pale crepe, the 15-85 copolymer exhibits tensile and elongation characteristics similar to those of similar blends containing the cyclized Pliolite.

The data of Table III show that blends of Pliolite S-3 and GR-S flow more readily at 212°, 220°, and 240° F than do similar blends of Pliolite and GR-S. The impact resistance of Pliolite S-3 resin is somewhat better than the impact

TABLE III

## FLOW CHARACTERISTICS OF PIIOLITE S-3 BLENDS WITH GR-S

Resin-rubber ratio	Flow test (seconds per inch)		
	212° F	220° F	240° F
70 Pliolite S-3-30 GR-S	17	13	2
90 Pliolite S-3-10 GR-S	40	19	5
70 Pliolite-30 GR-S	42	31	9
90 Pliolite-10 GR-S	203	150	60

TABLE IV

## IMPACT RESISTANCE OF PIIOLITE S-3 BLENDS WITH GR-S AND CREPE RUBBER

Resin-rubber ratio	Izod impact (inch-lb.)
90 Pliolite S-3-10 GR-S	3.0
90 Pliolite S-3-10 pale crepe	4.6
100 Pliolite S-3	2.2
90 Pliolite-10 GR-S	1.9
90 Pliolite-10 pale crepe	3.9
100 Pliolite	1.5

resistance of the cyclized rubber Pliolite. Likewise, blends of Pliolite S-3 with GR-S and with pale crepe, with no other compounding ingredients, have somewhat greater impact resistance than similar blends containing regular Pliolite. Milled sheets of Pliolite S-3 alone are fragile, but the addition of 10 parts of GR-S renders the resin more resistant to fracture on impact. Ten parts of pale crepe in Pliolite S-3 also impart excellent resistance to impact, despite its high hardness.

Since Pliolite S-3 has very low moisture absorption, blends of unusually low water absorption can be prepared by using deproteinized rubber or special GR-S types of low water absorptive characteristics. Typical master batches of 50 parts of Pliolite S-3 and 50 parts of special GR-S have a moisture absorption of approximately 2 mg. per square inch after 4 hours' soaking at 70° C, 5 to 8 mg. after 20 hours, 12 mg. after 48 hours, and 15 mg. per square inch after 96 hours in water at 70° C.

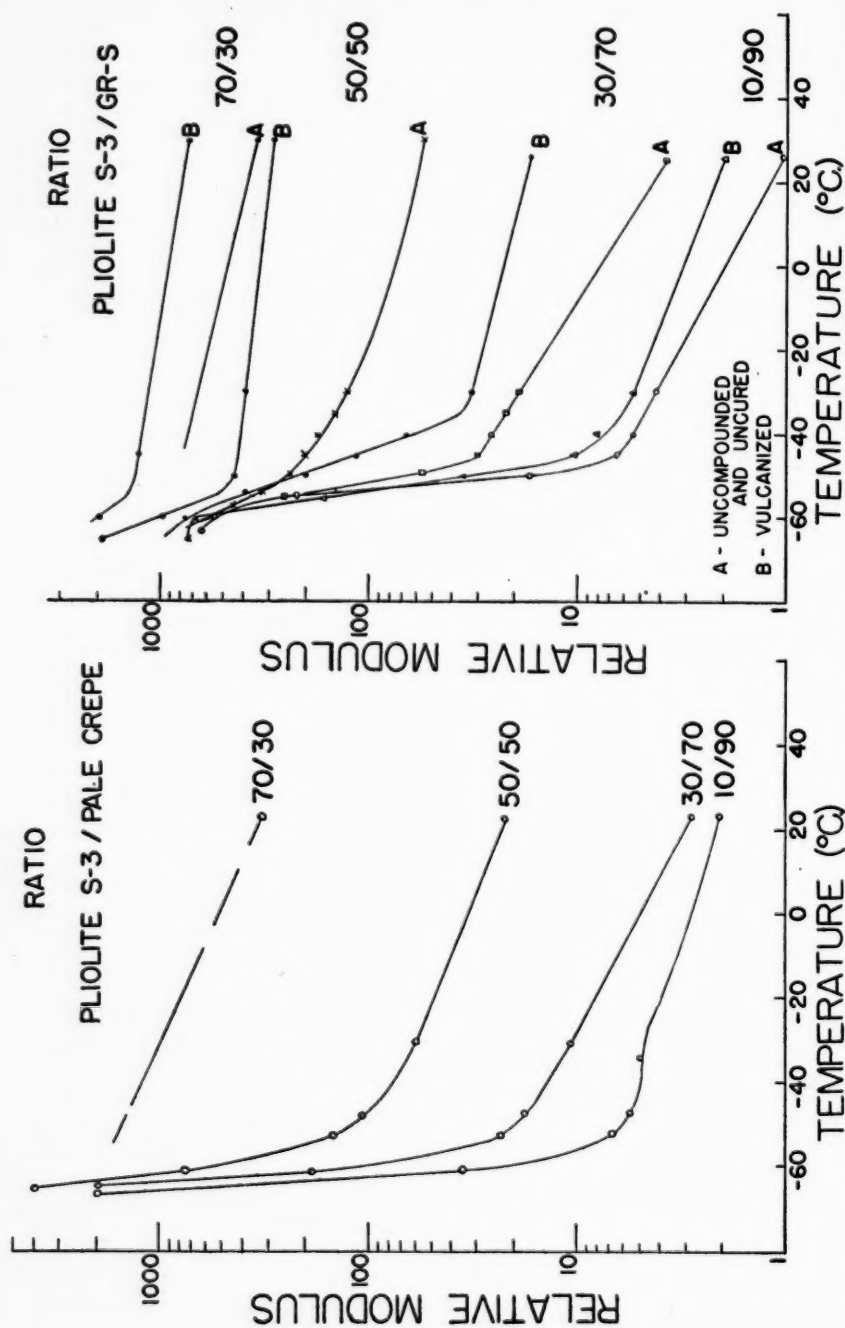


FIG. 1.—Torsional Modulus Data on Blends of Pliolite S-3 with Natural Rubber and GR-S

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The electrical properties of Pliolite S-3 were described earlier in the paper. In admixture with special types of GR-S of low water absorption, thus 15-85 copolymer is used as electrical insulation.

Table V lists the brittle points measured for mixtures of Pliolite S-3 with pale crepe and with GR-S. Incorporation of as much as 50 parts Pliolite S-3 per 100 part of total stock raises the brittle point only slightly in either GR-S or natural rubber blends. Vulcanization raises the brittle point only a little. Blends of 70 parts resin with 30 parts rubber display much higher brittle points, cured or uncured.

TABLE V  
BRITTLE POINTS OF RUBBER BLENDS WITH PLIOLITE S-3

Ratio of GR-S to Pliolite S-3	Cure at 320° F (min.)	Impact brittle point (° C)
90-10	Uncured	-57
	5	-57
	30	-51
70-30	Uncured	-57
	5	-57
	30	-51
50-50	Uncured	-57
	5	-46
	30	-46
50-70	Uncured	-12
	5	-23
	10	-23
	30	-23
90*-10	Uncured	-57
70*-30	Uncured	-57
50*-50	Uncured	-46
30*-70	Uncured	-7

\* Pale crepe in this series instead of GR-S.

To determine the effect of reduced temperatures on the stiffness of Pliolite S-3 blends with rubber, torsional modulus of several stocks was measured (Figure 1). Although increasing amounts of Pliolite S-3 increase the stiffness of rubber stocks at room temperature, the rate at which the relative modulus increases with lowered temperature is no greater for stocks containing larger amounts of Pliolite S-3. In agreement with the brittle point data, the temperature at which the relative modulus curve rises abruptly is not greatly different for blends containing 10 to 50 parts of resin in 100 parts of blend.

#### APPLICATIONS

The effectiveness of Pliolite S-3 as a stiffening agent for rubber and synthetic rubbers encourages its general use for increasing the hardness and rigidity of stocks and, at the same time, retaining a certain amount of resilience. This resin has been found useful as a stiffening and reinforcing agent in rubber and synthetic rubber footwear.

Because of its processing characteristics, dielectric properties, and low moisture absorption, 15-85 copolymer has found application in wire insulation. The reduction in the amount of shrinkage caused by the presence of the resin

makes possible close control of the gage of extruded wire insulation and permits accurate centering of the conductor.

Blends of Pliolite S-3 in certain proportions with synthetic rubbers have unique balatalike properties, and have been used to replace costly balata for certain articles such as golf ball covers. In most uses Pliolite S-3 serves equally as well as Pliolite and in many instances offers definite advantages to the cyclized rubber derivative. Pliolite S-3 is of particular interest in applications where ease of processing, resistance to oxidation, and uniformity are required beyond those offered by the older product.

#### EXPERIMENTAL PROCEDURES

The moisture absorption data were obtained by immersing  $1 \times 4 \times \frac{1}{16}$  inch samples in water at  $70^{\circ}\text{C}$  for 20 hours. The water absorption in milligrams per square inch was determined.

For determination of heat distortion points, molded strips,  $1 \times 10 \times 0.05$  inch, were suspended at the ends in a water bath. The middle of the strip was periodically deflected and held for 15 seconds at various temperatures. After the pressure was relieved and the strip removed from the water bath, the permanent set was checked by measuring the bow at the center. The temperature at which the bow reached  $\frac{1}{4}$  inch was said to be the heat distortion point.

Stiffness tests were run on the Olsen stiffness tester on  $0.590 \times 5.5$  inch samples after 24-hour conditioning at  $77^{\circ}\text{F}$  and 50 per cent humidity. The stiffness was recorded as the bending moment in inch-pounds.

Izod impact values were determined on notched bars. The units are inch-pounds per inch of face.

The flow characteristics were studied in a flow tester made by the Tinius Olsen Testing Machine Company. A pressure of 1500 pounds per square inch was used at three different temperatures. The flow is recorded as the seconds required for one inch of flow.

In the torsion cold test, five strips were mounted on a rack in an insulated cylindrical container. The temperature in the cylinder was controlled by regulating the volume of an air stream which blew across the dry ice in the bottom of the cylinder. The samples were attached in succession to a torsion wire and torsion head. The twist of each sample for a  $90^{\circ}$  twist of the torsion head was recorded as a function of temperature.

It should be understood that minor changes in the data of Table IV, as well as in the other tables of test results, could result from variations in the technique used in mixing the batches.

#### ACKNOWLEDGMENT

The authors are grateful to many members of the Goodyear Research and Chemical Engineering Divisions who aided in developing and testing of Pliolite S-3. The continued encouragement and suggestions of L. B. Sebrell and H. J. Osterhof were extremely helpful. The permission of the Goodyear Tire & Rubber Company for publication of this paper is appreciated.

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- <sup>2</sup> Bruson, British patent 306,390 (1923); U. S. patent 1,797,188 (1931).
- <sup>3</sup> Endres, U. S. Patent 2,052,391 (1936).
- <sup>4</sup> Thies and Clifford, *Ind. Eng. Chem.* **26**, 123 (1934).
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# THE THERMOPLASTICITY OF CHLORINATED RUBBER \*

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Up to the present time none of the work which has been devoted to improving the properties of chlorinated rubber, such as its stability, its plasticization, and the viscosity of its solutions, has, to the knowledge of the present author, taken into consideration its thermoplasticity. It seemed of interest, therefore, to look into this question.

Just as in the case of normal plasticity, it is difficult to measure thermoplasticity by any method which is not essentially empirical. This property is a complex one, and chlorinated rubber does not soften at a fixed temperature; in fact the softening temperature depends to a certain extent on the operating conditions.

In the present work an attempt has been made to treat this problem on a rational basis by studying the various factors involved in chlorination which influence in one way or another the thermoplasticity of chlorinated rubber.

## PREPARATION OF CHLORINATED RUBBER

Chlorinated rubber is formed by the action of chlorine on a solution of rubber; the chlorine reacts by simultaneous addition and substitution, thus:



In the experimental work, the chlorination reaction was carried out with a solution of 3 grams of slightly masticated rubber in 120 cc. of carbon tetrachloride. The solution, brought to its boiling point at 75° C, was agitated mechanically, and dry chlorine gas was passed into the point of saturation, which required about three hours. When chlorination was complete, the dissolved hydrogen chloride gas was expelled by heating the solution to the boiling point, and the rubber was freed of solvent by steam distillation.

After drying in an oven, approximately ten grams of a voluminous, white, flocculent, porous mass was obtained, the chlorine content and thermoplasticity of which were determined.

## DETERMINATION OF THE THERMOPLASTICITY

To determine the thermoplasticity, a pellet of the chlorinated rubber was molded in a small hand press, as represented in Figure 2. The press, containing 2 grams of chlorinated rubber, was kept for 20 minutes in an oven at 70° C. The chlorinated rubber, which had become plastic as a result of this heating,

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 21, No. 4, pages 83-84, April 1944.



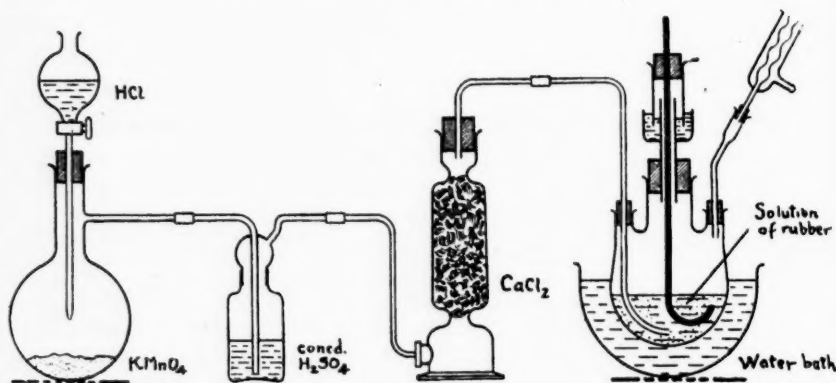


FIG. 1.—Assembly for preparing chlorinated rubber in the laboratory.

was compressed, and, after cooling in a current of compressed air, was removed from the press as a disc 20 mm. in diameter and 3 mm. thick.

To determine the softening temperature, the hardness of the disc was measured, by a Shore durometer, at prearranged time and temperature intervals, *viz.*, a temperature rise of 5° C each quarter hour in an oven.

As an arbitrary standard, the initial softening temperature was regarded as the temperature at which the Shore hardness decreased two units.

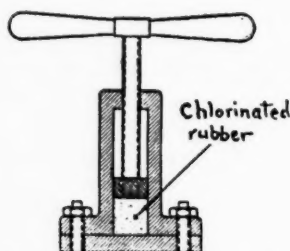


FIG. 2.—Press for molding chlorinated rubber.

### EXPERIMENTAL RESULTS

In the systematic investigation which was undertaken, it was deemed essential to vary at one time only one factor among those which were believed to be capable of affecting the thermoplasticity of the final product.

It might be remarked that it is rather difficult to prepare, even under the same conditions, two samples of chlorinated rubber with exactly the same properties. Appreciable differences have been found in two commercial products of the same brand, which were supposed to be alike. For this reason all experiments were carried out in duplicate.

**Percentage of chlorine.**—The thermoplasticity of chlorinated rubber decreases with increase in the percentage of combined chlorine. Incompletely chlorinated products are orange in color, are unstable, are very thermoplastic (softening around 80° C when the chlorine content is 50 per cent), and give highly viscous solutions. However, with increase in chlorine content, the

viscosity and thermoplasticity decrease, until, at about 60 per cent of combined chlorine, the thermoplasticity no longer changes significantly with increase in the combined chlorine.

*Nature of the rubber.*—When the impurities in the rubber are not too high, the type of rubber does not play any part in the thermoplasticity of chlorinated rubber made from it.

*Temperature* (see Figure 3).—The temperature of chlorination has a certain influence on the properties of the product, and it can affect by 20° C the softening temperature. Chlorine is more rapidly fixed at elevated temperatures, but in lower proportions than when the reaction is carried out cold. Chlorination at room temperature gives a product which contains relatively more combined chlorine and is relatively less thermoplastic. In this case, the reaction is exothermic, and there is a rise in temperature up to about 40° C.

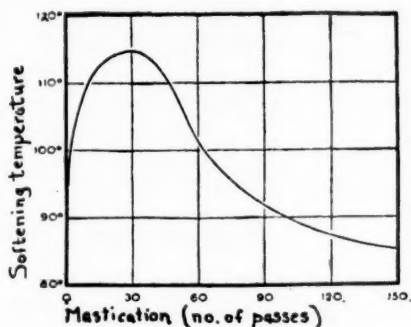


Fig. 3.—Influence of mastication of the original rubber on the thermoplasticity after chlorination.

*Nature of the solvent.*—Few solvents can be employed, for to be adaptable they must be resistant to the reaction of chlorine. Only chloroform and carbon tetrachloride were investigated. The former gave a product which was less thermoplastic than that obtained with carbon tetrachloride, but since in the former case chlorination was carried out at the boiling point, this difference can undoubtedly be explained by the difference in boiling temperatures of the solutions made up with the two solvents. This resolves, then, into the influence of temperature.

*Preliminary mastication of the rubber* (see Figure 4).—The thermoplasticity of chlorinated rubber is a minimum when the original rubber has been moderately masticated. This phenomenon can be explained: (1) by the fact that, although unmasticated rubber gives a chlorinated product which has relatively little thermoplasticity, the solution has initially a very high viscosity and is difficult to chlorinate; and (2) rubber which has been masticated to a high degree gives a thermoplastic chlorinated rubber but its solution is highly susceptible to chlorination.

*Light.*—As in the chlorination of the majority of organic compounds, light promotes the fixation of chlorine on rubber.

By taking advantage of the facts described above, and with a view to preparing a chlorinated rubber with the least possible thermoplasticity, the chlorination reaction was carried out on: (1) slightly masticated rubber (25 passes through a mill); (2) at cold temperature and with exposure to light; and (3) by

treatment with chlorine until the final product contained at least 60 per cent of combined chlorine.

By operating in this way, a chlorinated rubber was obtained which had a thermoplasticity similar to that of commercial products. In an attempt to reduce this thermoplasticity, efforts were made to chlorinate a solution of unmasticated rubber, the viscosity of which had been made particularly low by one of three means: (1) by using a low concentration of rubber; (2) by choosing a solvent which gave a solution of relatively low viscosity, and (3) by adding a polar solvent.

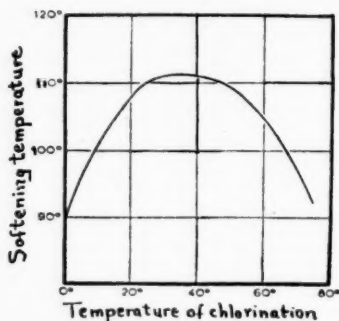


FIG. 4.—Influence of the temperature of chlorination on the thermoplasticity of the chlorinated rubber.

This last alternative did not give satisfactory results because of the difficulty in finding a polar solvent which was inert to the action of chlorine. On the other hand, when the chlorination was carried out with 1.5 per cent solutions of unmasticated first-latex crepe, the chlorinated rubber obtained was found to be slightly less thermoplastic, *i.e.*, it had a softening temperature 10° C higher, than that of commercial chlorinated rubber, and was just as stable<sup>1</sup>, although the former contained no stabilizing agent.

### CONCLUSIONS

Among the various factors which play a part in the chlorination of rubber, the percentage of combined chlorine, the temperature of chlorination, and the degree of mastication have pronounced effects on the thermoplasticity of the final chlorinated rubber products. By taking advantage of certain operating conditions which are suggested by the work described above, it is possible to obtain a chlorinated rubber with relatively low thermoplasticity.

It does not appear to be possible by these means to reduce to any significant degree the thermoplasticity of chlorinated rubber, without perhaps the use of operating conditions which would be difficult to control, *e.g.*, chlorination under pressure or at high temperature.

### REFERENCE

- <sup>1</sup> The stability was measured by the method of Nielsen, *i.e.*, heating for 5 minutes at 100° C in concentrated sulfuric acid (cf. Nielsen, *Paint Manuf.* 6, 153 (1936)).

## ABRASION TESTS ON RUBBER \*

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### INTRODUCTION

Although the abrasion machine to be described has been used in the laboratories of the British Boot, Shoe and Allied Trades Research Association for many years, there has been no publication of a description, nor any account of its performance. The original machine has been modified by the incorporation of an efficient suction device, and redesigned structurally, though still employing the same basic mechanism. Experiments have been carried out on large numbers of war-time substitutes for soling-leather, rubber-soling materials with reduced rubber content, for containing GR-S, and new plastic materials and synthetic rubbers. The machine has been found to give reproducible figures, quickly and under easily controlled conditions, and the results have been of value for comparing various materials. No attempt is made in this paper to judge the significance of these figures or to correlate them with actual wear data.

### DESCRIPTION OF ABRASION MACHINE

Figure 1 gives a diagrammatic view of the machine. The framework is of 2-inch angle iron, rigidly bolted together, carrying a  $\frac{1}{4}$  h.p. electric motor, which drives pulley A on the main countershaft. This has a triple cone pulley, driving one of the three large pulleys at B by means of twin V-belts, so as to provide speeds in the ratio of 1:2:4, as desired. The spindle carrying these large pulleys also carries a gear wheel which engages with the gear wheel C. The crank shaft E gives a translatory motion to the carriage F, which travels on accurately machined guides on the grid structure G. The carriage makes 25 double strokes or traverses per minute, and the length of each stroke is 3 in.

Figure 2 shows the details of the arrangement for holding the specimens. A rectangular bar H,  $7\frac{1}{4}$  in.  $\times$  1 in.  $\times$   $\frac{3}{4}$  in. thick, is rigidly connected to F, and the two recesses in the underside of this bar contain the samples to be tested, which are 1 inch square, and 0.20 to 0.25 inch in thickness. Resting on each same is a square metal plate of the same area, attached to a vertical rod which is free to move up and down. The top end of this rod makes contact with the micrometer dial gauges. By means of these the changes in thickness of the samples can be measured (to 0.01 mm.) while the machine is running. This obviates the necessity of stopping the machine at intervals to take thickness measurements or weighings. A lever system attached to each vertical rod enables a load of 8 pounds to be applied to each sample; this gives a pressure of the same order as that on a shoe sole during wear. The lever system is so designed that the effective load remains approximately the same throughout a test run, even though the lever arm drops slightly as

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 6, pages 375-390, April 1946.

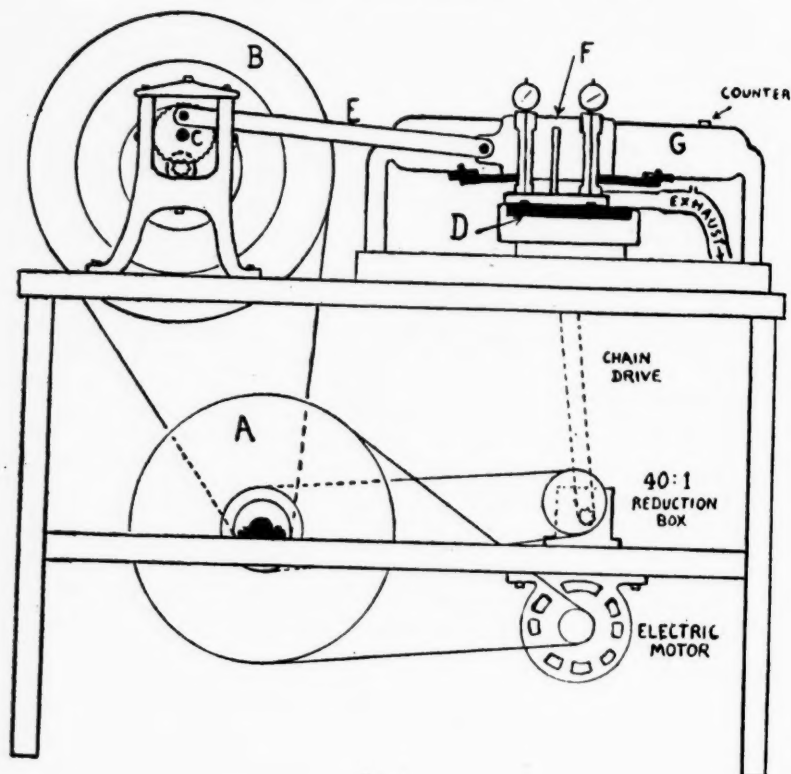


FIG. 1

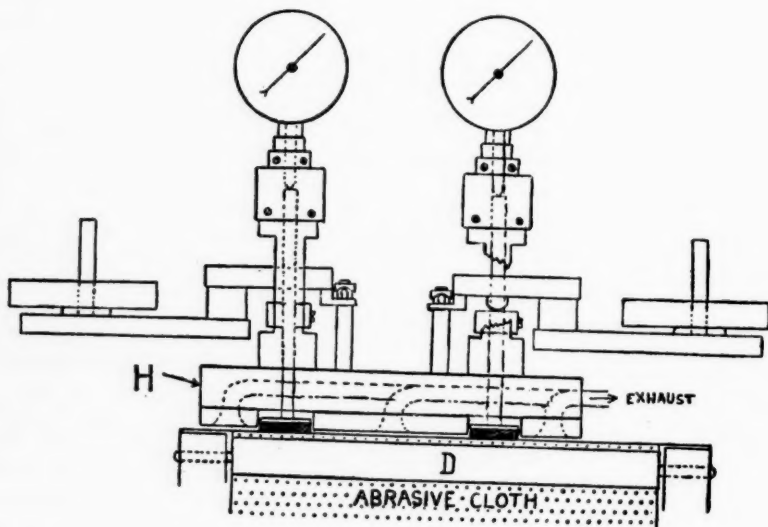


FIG. 2

the thickness of the sample decreases. In addition the low center of gravity of the system ensures maximum stability and absence of side thrust.

Bar H has been drilled in three places, as shown, and metal tubes lead from these to a wider tube connected to a suction device, *i.e.*, a dust extractor. There is thus a cleaning arrangement in front of, and behind each sample, as it travels backwards and forwards over the 8-inch wide abrasive cloth (standard 80XCL Durexsil), which is drawn slowly over the flat bed of the machine. This bed, which is  $10 \times 2$  inches in area, has been machined accurately parallel to the guides on G. The abrasive cloth is not shown in Figure 1, for reasons of clarity, but a 25-yard roll is mounted at the front of the machine. The cloth is fed under rubber roller D, then over the flat bed, and is finally gripped in a clamp attached to a split nut, which engages a threaded rod 15 inches long, driven by a chain from the 40:1 reduction box. The latter has a belt drive from the main countershaft. When the clamp reaches the end of the threaded rod it must be disengaged and moved to its original starting position. The length of this threaded rod is more than sufficient for three complete tests. The clamp travels at 0.42 inch per minute, so that in a test run of 250 strokes in 10 minutes the length of abrasive cloth used is 4.2 inches. Bar H and the lever systems can be raised and lowered for the insertion and removal of specimens by means of a screw head on the carriage F, but, of course, it is always kept at the same height during a test. A counter fixed to G records the number of double strokes of the carriage F, that is, the number of complete to-and-fro movements. Hereafter double strokes are referred to as strokes.

The procedure for a routine test is as follows. The buffed samples are inserted in the machine, which is then run for five to ten strokes to "bed down" the samples. In practice five strokes are sufficient and the counter is set at 95. The first readings of the dial gauges are taken at 00 on the counter, and then for every fifty strokes afterwards. The left hand gauge is read at its minimum position when the carriage is moving towards the right, and then the right hand gauge is read at its minimum position when the carriage is moving to the left. In this way readings for each side are taken at 0, 50, 100, 150, 200, and 250 strokes. The differences from the reading at 0 give the decreases in thickness (in millimeters) for the corresponding number of strokes. If the decrease in thickness is plotted against the number of strokes, the graph is a straight line for rubber or any other homogeneous material. In these cases it is sufficient to proceed with the test for 250 strokes only, calculating the loss in thickness for 250 strokes by subtracting the final from the initial reading of the thickness, and multiplying by 4 to obtain the rate in mm./1,000 strokes. Generally, there is little difference between the results for left- and right-hand sides, so the losses in thickness for 250 strokes for each specimen are added together and the sum is doubled to give the rate in mm./1,000 strokes.

Typical values for the rates of abrasion of good quality rubber composition soling materials lie between 7.0 and 9.0. The prewar average of rubber composition sheeting was about 8.5 mm. per 1,000 strokes. When the quality of sheeting was of lower standard than that of the present time, *i.e.*, before the introduction of GR-S, the figures were between 10 and 14, and sometimes higher. The present average is about 9.0. The standard rubber mix, mentioned later, gives values between 5.0 and 5.5 mm. per 1,000 strokes. The lowest rates of abrasion obtained were 2.5 for a canvas-rubber belting, and 2.8 to 3.4 for several samples of polyvinyl chloride, and the highest rate was 31 for a cork and rubber material.



## PHYSICAL PROPERTIES OF THE RUBBER

*Composition sheeting.*—The plain rubber sheeting for these investigations was just above the minimum standards for the Rubber Sheeting Specification. Though its rate of abrasion was rather high, it was chosen because of its uniformity along and across the sheet, and because it showed no great deterioration after aging. This sheet was about 29 inches square, and was used for tests A to E mentioned below. A second sheet of rubber, of the same manufacture and closely similar in properties except for thickness, was used for the test F. A third sheet, also from the same source, but thicker, was used for the test G. The main physical properties of these sheets are shown below, together with the minimum standards for the Rubber Sheeting Specification.

TABLE 1

Properties	1st Sheet for Tests A-E		2nd Sheet for Test F		3rd Sheet for Test G		Specification Standards		
	Normal Aged		Normal Aged		Normal Aged		Normal Aged		
Thickness (mm.)	5.1		4.0		6.1				
Density (g. per cc.)	1.36		1.31		1.31				
Tensile strength (kg. per sq. cm.)	<i>Along</i>	75.0	78.1	78.6	78.0	85.0	89.3	<63.3	<63.3
	<i>Across</i>	74.4	73.4	73.7	75.1	79.5	81.5	<63.3	<63.3
Breaking strain (per cent)	<i>Along</i>	165	110	185	125	235	160	<150	<100
	<i>Across</i>	163	112	195	120	250	160	<150	<100
Permanent set (per cent)	<i>Along</i>	6.5	7.0	6.0	4.5	4.0	3.0	>7.5	>7.5
	<i>Across</i>	6.0	5.5	6.0	5.0	3.0	3.0	>7.5	>7.5
Rate of abrasion (mm. per 1000 strokes)	9.4		10.0	9.6	10.3	10.5	9.5		
Abrasive index				59	55	54	60	<50	<50
B.S. hardness number (thickness mm.)				32	27	36	30	20-40	15-40
				(3.7)	(3.8)	(5.9)	(5.8)		

All the tests were carried out in a room maintained at a temperature of  $21 \pm 0.5^\circ \text{C}$ , and  $75 \pm 2$  per cent relative humidity.

Figure 3, not drawn to scale, shows how the first abrasive roll, 25 yd.  $\times$  8 in. wide, and the first part of a second roll, were utilized for the tests which follow.

The letters L to Q represent the various locations, equally spaced along the rolls, used in Test A, the experiments being carried out when these places were reached. Tests B to E were performed in the positions indicated on the plan, while the remainder of the roll was used for routine testing, unconnected with this research. Test F, for the variation of rate of abrasion with grade of abrasive, was carried out on seven different grades of abrasive cloth, each about 28 inches long, using the second sheet of rubber. Finally, Test G, for the reduction of cutting power of the abrasive due to repeated use, i.e., the decrease in

## PLAN OF TESTS

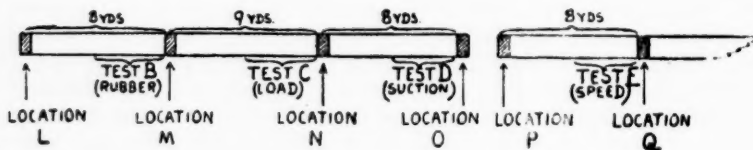


Fig. 3

the rate of abrasion with repeated use, was performed on a short length of cloth, approximately 10 inches long, taken further along the second roll.

*Test A. Variability of Abrasive Cloth.*—A rectangle, 6 by 10 inches, was cut from the first sheet of rubber, and divided into 60 separate one-inch squares, which were numbered 1 to 60 before cutting out with a sharp knife. Great care was taken to keep the sides of the squares normal to their faces. Measurements were made of the lengths of the edges of the top and bottom faces, and showed that the edges of the squares were mostly 1.00 inch long, and rarely were greater than 1.01 or less than 0.99 inches. In addition, all the separate squares were weighed and the thicknesses measured, before and after test. This procedure was carried out as a precaution in all tests, though calculations based on losses in weight showed no significant difference from those obtained by the usual method of losses in thickness, which method is certainly simpler and more direct, and can be carried out while the machine is in motion, without the necessity of frequent stoppages for weighings.

As can be seen from the plan, there were four locations on the first roll, and two on the second roll. The sixty one-inch squares provided thirty pairs of originally adjacent squares, and these were randomized into six groups of five pairs, in order to minimize errors due to variability of the rubber. One

TABLE 2  
TEST A. MM. PER 500 STROKES

	Group L	Group M	Group N	Group O	Group P	Group Q
	4.40	4.39	4.30	4.55	5.18	5.32
	4.14	4.57	4.86	4.48	5.36	5.44
	4.92	4.22	5.09	4.84	5.27	5.39
	4.78	4.40	4.75	4.49	5.48	5.21
	4.55	4.39	4.83	4.40	5.32	5.45
Mean	4.558	4.394	4.766	4.552	5.322	5.362
Standard error	±0.138	±0.055	±0.130	±0.076	±0.050	±0.044

group was chosen at random for each location, and the pairs in each group were randomized for order of testing. Commencing with location L, each of the five pairs in this group was tested on the abrasion machine for 250 strokes. The sum of the loss in thickness of the left and right specimens of each pair is taken as the rate of abrasion for that pair, expressed in mm. per 500 strokes. The other groups were then tested when the appropriate positions on the abrasive rolls were reached. Table 2 shows the rates of abrasion for each of the five pairs in the six locations L to Q.

The 5 per cent point for  $z$  when  $n_1 = 3$ ,  $n_2 = 16$  is at 0.5876, so the observed value is not significant, *i.e.*, there is no significant difference between the locations L, M, N and O, on the first roll of abrasive cloth, and the extent to

TABLE 3  
ANALYSIS OF VARIANCE FOR GROUPS L, M, N, O

Source of variation	Sum of squares	Degrees of freedom	Variance
Between groups	0.34917	3	0.11639
Within a group	0.8918	16	0.5574
Total	1.24097	19	

$$z = 0.5 \log_e \frac{0.11639}{0.5574} = 0.3682$$

which they differ can be attributed to random sampling. In other words, this experiment gives no indication that parts of the abrasive cloth widely separated on the roll differ appreciably more than those which are close together.

The mean of groups L, M, N, and O is 4.5675, and the mean of groups P and Q is 5.342. The difference between these is about 12 times the square root of the sum of the squares of the standard errors of the means, and clearly shows a significant difference between groups L, M, N, O and P, Q. In other words, the second roll of abrasive cloth differs appreciably from the first roll. Allowance for such differences between rolls of abrasive for routine testing, is made in the following manner.

Supplies of a standard rubber mix, in sheet form, are used for calibrating each roll of abrasive. The mix has the composition given in Table 4.

TABLE 4

First quality smoked sheet rubber	100	} Cure, 25 min. at 153° C
MPC Black (Dixie)	60	
Whiting	60	
Mercaptobenzothiazole	1	
Zinc oxide	4	
Stearic acid	3	
Witcoplas	3	
Sulfur	3	
Phenyl-beta-naphthylamine	1	

This material has a rate of abrasion between 5.0 and 5.5 mm. per 1000 strokes.

Eight pairs of abrasion squares are tested in the usual manner at the commencement of each new length of abrasive cloth, and the mean rate of abrasion of these specimens is taken as the standard rate for that roll. This figure, in mm. per 1000 strokes, is divided by the corresponding figure obtained for every rubber subsequently tested in routine work on this same roll of cloth. The ratio expressed as a percentage is termed the Abrasive Index (see Table 1) of the rubber under test. Check determinations on the standard rubber, carried out near the middle of the roll, and also near the end, have shown no significant difference from the original rate for that roll. For every fresh roll of abrasive cloth a new determination of the standard rate is carried out, and used to calculate the abrasive indices of all rubbers tested on that roll. In a few cases, where the same rubber has been tested on two different rolls, the values of the abrasive index have been found to agree within one or two per cent.

*Test B. Variability of Rubber Sheet.*—A square of rubber measuring 4 by 4 inches was cut from near each of the four corners of the rubber sheet. Each was divided into sixteen squares of one-inch side, keeping adjacent squares together in pairs. The four positions on the original rubber sheet are referred to as locations I, II, III and IV, each location providing eight pairs of adjacent squares. As in Test A, great care was taken in the cutting out to keep the sides of the squares normal to their faces.

One pair of squares was chosen at random from each location, and tested on the abrasion machine for 250 strokes, the order of testing being also randomized. This was repeated until all the pairs had been used, the randomization serving to minimize slight errors due to variability of the abrasive cloth. Table 5 below shows the rates of abrasion for the 32 pairs, in mm. per 500 strokes, obtained by adding the loss in thickness for 250 strokes for each of the two specimens in a pair.

The greatest difference in means is between III and IV, but is not significant. The value of  $z$  is 0.2120. The 20 per cent point for these degrees of freedom is at 0.2509; thus the observed values are not significant. These results would occur oftener than once in five times as a result of random sampling, and there is no evidence that specimens from locations far apart within the sheet differ more than do adjoining ones.

It may be noted in passing that if the values of the rates of abrasion in Table 5 are plotted against the order of testing, the graph shows a gradual rise in the mean rate from 4.5 to 4.8 mm. per 500 strokes, over a length of 11 feet of abrasive cloth. This is attributed to a slight variation of the abrasive itself, and is consistent with the magnitude of the variations revealed in test A.

TABLE 5  
TEST B. MM. PER 500 STROKES

Location I	Location II	Location III	Location IV
4.42	4.68	4.70	4.33
4.83	4.71	4.83	4.92
4.86	4.74	4.76	4.84
4.50	4.70	4.87	4.60
5.19	4.69	4.67	4.61
4.83	4.68	4.50	4.42
4.56	4.53	5.01	4.41
4.58	4.67	4.72	4.44
Mean	4.721	4.675	4.571
Standard error	$\pm 0.090$	$\pm 0.022$	$\pm 0.054$

TABLE 6  
ANALYSIS OF VARIANCE

Source of variation	Sum of squares	Degrees of freedom	Variance
Between locations	0.1565	3	0.0522
Within a location	0.9565	28	0.03416
Total	1.1130	31	—

*Test C. Variation of Rate of Abrasion with applied Load.*—In this test there were 34 pairs of originally adjacent 1-inch squares cut from a rectangle 6 × 12 inches providing eleven pairs for the lowest and highest loads, and twelve pairs for normal load. All the squares were chosen at random for these three groups, and the order of testing was obtained by randomizing eleven sets of three treatments for load, finishing with one pair extra for normal load. Thus, any differences due to variations in the rubber, or a progressive change in the abrasive cloth, were minimized.

The various loads were obtained by altering the masses attached to the lever systems, and measuring directly the downthrusts in each case. For the lever system, the experimental relationship between the applied mass and the resulting downthrust (which is equal to the load in lbs. per sq. in.) was found to be:—Load (lbs. per sq. in.) =  $2.25 + 5.05 \times \text{mass applied (lbs.)}$ .

In Table 7 below, the rates of abrasion, in mm. per 500 strokes, are quoted for the pairs of squares for each of the three loads.

The ratio of loads between groups is in each case greater than the corresponding ratio for rates of abrasion, indicating that the rate of abrasion increases less rapidly than the load. This is shown in Figure 4, where the rate

TABLE 7  
TEST C. MM. PER 500 STROKES

	Load (2.25 lbs. per sq. in.)	Normal load (8.00 lbs. per sq. in.)	Load (12.89 lbs. per sq. in.)
	1.41	4.54	6.99
	1.41	4.71	6.80
	1.40	4.42	5.95
	1.30	4.04	5.92
	1.39	4.07	6.30
	1.19	4.20	5.97
	1.32	3.97	5.87
	1.19	3.99	6.02
	1.14	3.97	6.10
	1.13	3.97	5.99
	1.34	4.13	6.10
	—	4.16	—
Mean	1.293	4.181	6.183
Standard error	$\pm 0.033$	$\pm 0.071$	$\pm 0.111$

of abrasion tends to reach a limiting value for high loads. This graph is not linear and falls away more and more from a straight line as the load is increased. The equation of the curve drawn through the three points and the origin is:

$$\text{Rate of abrasion (in mm./1000 strokes)} = 33.3(1 - e^{-0.0362x})$$

where  $x$  is the load applied, in lbs. per sq. in.

*Test D. Effect of Suction.*—A water manometer, attached to the exhaust tube near the point where it leaves the travelling carriage F (Figure 1) enables the determination of the pressure in the exhaust system to be made while the machine is running or stationary. It also enables the suction to be maintained constant for all experiments, and set at a definite value. Previous work had indicated that the effect of suction was approximately constant over a

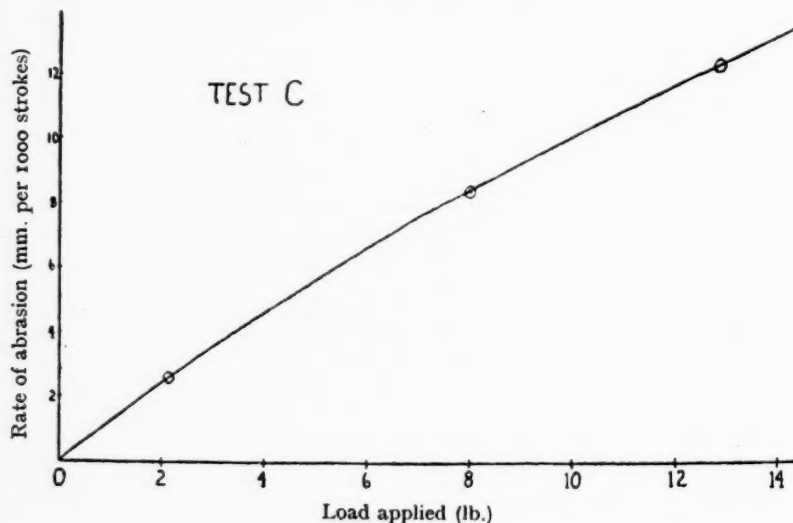


FIG. 4

wide range, yet with no suction at all, the rate of abrasion was roughly halved. It appeared that a vacuum pressure of only about 5 cm. of water was sufficient to remove most of the abraded particles. It was decided, therefore, to adjust the exhaust air flow to give the following vacuum pressures, 4 cm., 10 cm., and 30 cm. of water. With the addition of a group for testing without suction there were thus four groups. In the same way as for previous tests, thirty-two pairs of adjacent 1-inch squares were cut from a rectangle 6 × 11 inches in the original rubber sheet. These were randomized into the four groups to counteract, as much as possible, any variation in the rubber. To minimize the effects of variability in the abrasive cloth, the eight pairs in each group and the sequence of groups, were randomized for order of testing. Table 8 gives the rates of abrasion (in mm. per 500 strokes) for the four groups. Unfortunately, one pair from the first group was tested without suction, and was thus transferred to the last group.

TABLE 8  
TEST D. MM. PER 500 STROKES

	Group 1 30 cm. water	Group 2 10 cm. water	Group 3 4 cm. water	Group 4 0 cm. water
	4.53	4.37	4.12	2.14
	4.23	4.49	4.19	2.15
	4.49	4.28	3.95	2.15
	4.73	4.66	4.34	2.11
	4.44	4.54	4.04	2.21
	4.55	4.48	4.07	2.06
	4.53	4.56	3.61	2.11
		4.23	3.77	2.13
				1.98
Mean	4.500	4.451	4.011	2.116
Standard error	±0.056	±0.052	±0.082	±0.022

Calculation shows that the means of groups 2 and 3, as well as of groups 3 and 4, differ significantly, whereas the means of groups 1 and 2 do not. The data relating to the latter therefore suggest that the rate of abrasion increases slightly when the suction increases from 10 to 30 cm., but the increase, if real, is certainly very small.

Graph 2 (Figure 5) shows the rate of abrasion plotted against the vacuum pressure (cm. of water) and indicates clearly that an air flow producing a vacuum of 10 cm. of water in the exhaust tube is just sufficient to remove all the abraded dust. Increasing the air flow by speeding up the exhaust fans does not appreciably increase the rate of abrasion. On the other hand, below 10 cm. of water, the rate of abrasion falls off rapidly with decrease in air flow, finally reaching, at zero flow, a value about one half the maximum value.

For routine testing, the air flow is adjusted to give 30 cm. of water, which is well beyond the critical value, yet easily obtained and held steady over long periods. A rate of flow of about 3 liters per second produces a vacuum pressure of 10 cm. water, and thus, for a pressure of 30 cm., the air flow will be of the order of 5 liters per second (assumed to be proportional to the square root of the pressure). This rate is equivalent to an air speed of the order of 40 meters per second over the surface of the abrasive cloth.

Experiments with a large number of various types of rubber sheets have shown that the value of the ratio:

$$\frac{\text{rate of abrasion without suction}}{\text{rate of abrasion with full suction}}$$



lies between 0.4 and 0.6 for nearly all black rubber composition sheetings, the average value of the ratio being about 0.5. For very hard rubbers which give a fine dust when abraded, this ratio is constant at a value of about 0.7, showing a smaller increase in the rate of abrasion when suction is applied to remove the dust. From this it appears that the fine dust is not so effective in clogging the abrasive and thus reducing its cutting power. On the other hand, the soft rubbers give a value of less than 0.4 for the ratio, and the rate of abrasion increases to over two and a half times when suction is applied. This larger increase is due to the fact that these soft rubbers abrade into small cylindrical

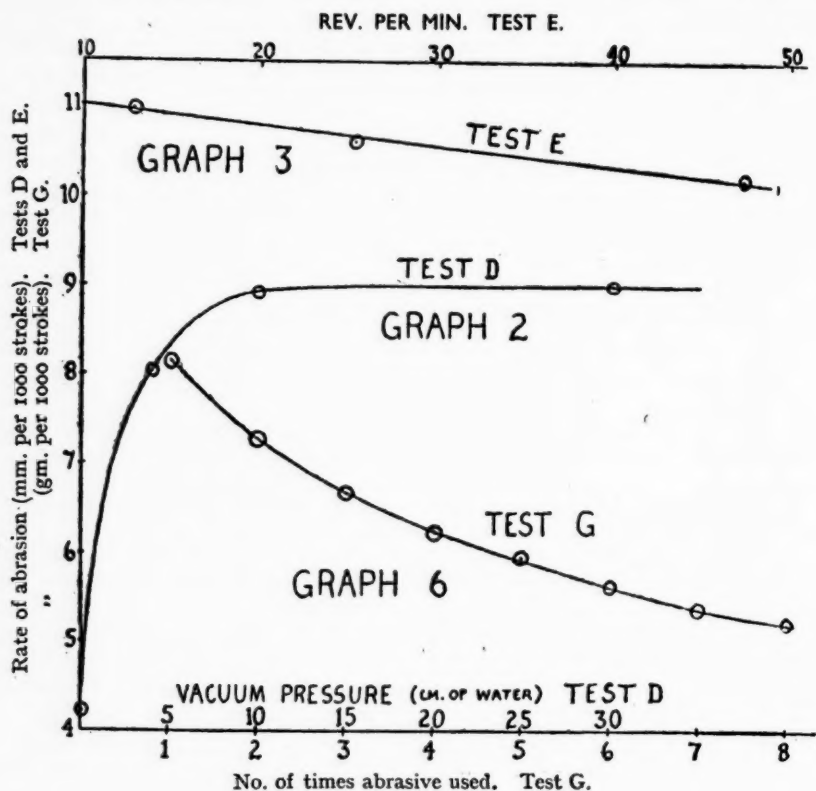


FIG. 5

rolls, over which the specimens travel to and fro, out of contact with the abrasive surface. The rate of abrasion obtained without suction is, therefore, too low, but the application of suction easily removes these miniature rolls, and allows the rubber to be abraded on the surface of the abrasive.

**Test E. Effect of Speed.**—By using in turn each of the three pairs of rubber V-belts driving the large triple cone pulley B (Figure 1) it is possible to run the crank wheel C at any one of these speeds, 12.8, 25.4 or 47.3 rev. per min. These are the number of strokes per minute of the specimens across the abrasive in the three cases, referred to below as groups 1, 2 and 3. It must be remembered that the speed at which the abrasive cloth is drawn through the machine

is the same in each case, the slowing down of the electric motor under the greatest load at the greatest speed being negligible. The principal effect of increasing the speed is thus likely to arise from the fact that, at the higher speeds, each part of the abrasive is used for a greater number of strokes of the machine, and therefore subjected to a greater blunting action, with consequent reduction of cutting power.

From a rectangle  $9 \times 8$  inches, 36 pairs of adjacent 1-inch squares of rubber were cut, and randomized into three groups, 1, 2, and 3, to minimize effects due to variation of the rubber in this rectangle. The order of testing of the thirty-six pairs was obtained by randomizing the numbers 1, 2, and 3, twelve times, so as to reduce errors arising from any variation of the abrasive along the roll of cloth. One of the twelve pairs in group 2 was damaged, and had to be discarded. The results are shown in Table 9.

TABLE 9  
TEST E. MM. PER 500 STROKES

	Group 1 Slow speed (12.8 r.p.m.)	Group 2 Normal speed (25.4 r.p.m.)	Group 3 Fast speed (47.3 r.p.m.)
	5.29	5.19	5.00
	5.20	4.98	5.37
	5.84	5.24	5.19
	5.68	5.71	4.81
	5.43	5.22	4.96
	5.85	5.25	4.82
	5.62	5.46	5.18
	5.09	5.78	4.95
	5.15	5.24	5.36
	5.47	4.84	5.40
	5.63	5.20	4.66
	5.60		5.50
Mean	5.488	5.283	5.100
Standard error	$\pm 0.075$	$\pm 0.084$	$\pm 0.079$

TABLE 10  
ANALYSIS OF VARIANCE FOR GROUPS 1, 2, 3

Source of variation	Sum of squares	Degrees of freedom	Variance
Between groups	0.902	2	0.451
Within groups	2.327	32	0.0727
Total	3.229	34	—

$$Z = 0.9126$$

The differences in means of groups 1 and 2, and also groups 2 and 3, are not significant, but the difference between groups 1 and 3 is significant.

The 1 per cent point is at 0.84; hence the observed values are significant of a real difference between the rates of abrasion of the three groups.

Graph 3 (Figure 5) shows the slight decrease in rate of abrasion with increase in speed, but since at the greatest speed the length of abrasive used is about one-fourth of that used for the slowest speed, it is concluded that, even at the greatest speed, fresh abrasive cloth is being fed into the machine sufficiently fast to prevent appreciable blunting or reduction in cutting power. The speed of the abrasive cloth is not critical in this range.

*Test F. Variation with Different Grades of Abrasive.*—Seven lengths of abrasive cloth,  $28 \times 8$  inches wide, of the following grades, 30X (very coarse),

TABLE 11

	Group 1 30X	Group 2 50X	Group 3 80X	Group 4 100X	Group 5 150X	Group 6 180X	Group 7 220X
	5.31	5.55	4.55	3.20	1.81	1.59	1.39
	5.80	5.73	4.37	2.81	1.86	1.77	1.40
	5.59	6.10	4.33	3.00	1.83	1.84	1.29
	5.73	5.80	4.53	3.40	1.94	1.64	1.36
	5.15	5.31	4.44	3.13	1.94	1.78	1.31
	5.33	6.03	4.38	2.98	1.80	1.70	1.20
		5.95					
Mean	5.485	5.781	4.433	3.087	1.863	1.720	1.325
Standard error	$\pm 0.106$	$\pm 0.106$	$\pm 0.038$	$\pm 0.083$	$\pm 0.026$	$\pm 0.038$	$\pm 0.031$

50X, 80X, 100X, 150X, 180X, and 220X (very fine) were used in turn on the abrasion machine in place of the usual long roll of 80X cloth. From a rectangle  $8 \times 11$  inches, taken from the second sheet of rubber, forty-three pairs of adjacent 1-inch squares were cut, and randomized into seven groups corresponding to the seven grades. The extra pair was allotted to the second group since the strip of 50X abrasive cloth was slightly longer than the others. The whole of each length was used for test, except for a few inches at the ends. The randomization into groups served to minimize the effects due to possible variation in the rubber. The order of testing in each group was also randomized. Table 11 gives the rates of abrasion obtained for the 6 pairs in each group.

Graph 4 (Figure 6) shows the relationship between rate of abrasion and grade of abrasive, indicating a decrease which roughly follows the dotted rectangular hyperbola. This curve closely agrees with that obtained in other

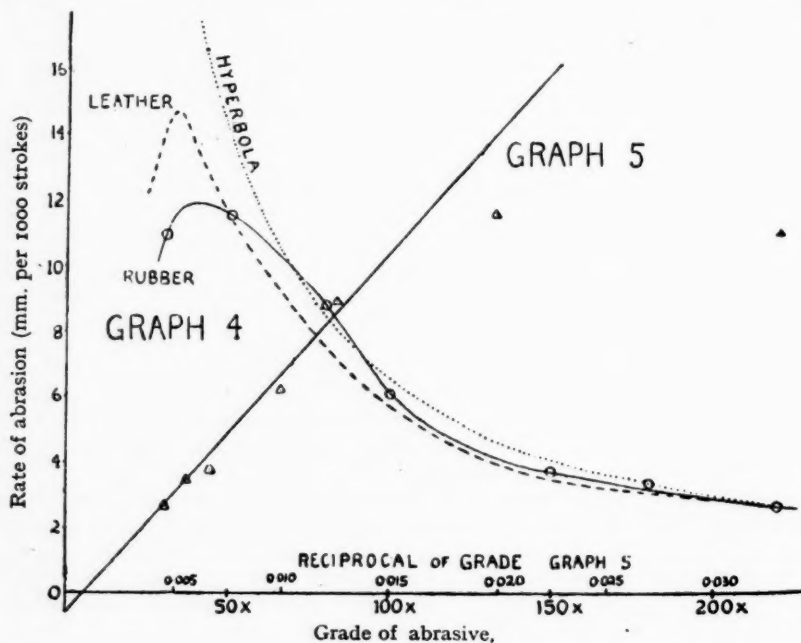


FIG. 6

work in these laboratories with leather without suction if the rates for the leather are doubled. In other words, the effect of changing the grade of abrasive is similar whether leather or rubber is being abraded. The curve shows a maximum between 30X and 50X, while for the coarser abrasives beyond 30X, the rate of abrasion decreases, apparently because the load of 8 lbs. per sq. in. on the samples is not sufficient to cause full penetration of the abrasive particles into the rubber for these coarser grades. It is probable that with a greater load, the maximum of the curve would be shifted towards the left. For leather, the maximum was found to occur at 34X.

The rate of abrasion is plotted on Graph 5 (Figure 6) against the reciprocal of the grade, and shows a linear relationship except for the two points corresponding to 30X and 50X, the former being quite distant from the graph.

The equation of this line is:  $y = \frac{730}{\text{grade}} - 0.7$ , where  $y$  is the abrasion rate in mm./1000 strokes. A similar result is obtained if the rate of abrasion is plotted against the size of aperture of sieve for each grade.

*Test G. Decrease in Rate of Abrasion due to repeated use of the same Abrasive.*—This test differed from the first six tests, in that, for reasons explained below, the losses due to abrasion were determined by loss in weight for 50 strokes instead of by decrease in thickness.

A 4-inch square was cut from the third sheet of rubber, and divided up into sixteen 1-inch squares, making eight pairs of adjacent squares, which were numbered 1 to 8. All were conditioned for twenty-four hours, and weighed. The test was arranged so that each pair was abraded in turn for 50 strokes exactly; then the abrasive cloth was returned to its starting position, and the pairs were again abraded, in a different order, for exactly 50 strokes again. This process was repeated until this one part of abrasive cloth (about 10 inches long) had been used eight times. The order of testing was obtained from a randomized  $8 \times 8$  Latin square, so that each pair of specimens was used once, and only once, on each of eight adjoining parts of the abrasive cloth. Thus, the effects due to any progressive change along the length of abrasive, and variation in the rubber, were minimized. As the specimens might not bed down properly immediately on insertion into the machine, and since no preliminary strokes could in this test be allowed, the abrasion losses were found by weighing instead of by measurements of thickness.

A white line was drawn across the abrasive cloth, and a spare pair of 1-inch squares was abraded, starting from this line, for 100 strokes, using about  $1\frac{1}{2}$  inches of cloth. This was necessary to ensure that the first of the eight pairs received the same treatment as the subsequent seven pairs, each of which, when first inserted into the machine would be in contact with abrasive which had previously been abrading the preceding specimen. Similarly, after the eighth pair, another spare pair was used for 100 strokes, at the end of which a second white line was drawn across the cloth. The eight pairs were weighed and the cloth was pulled back to the position of the first white line. The process was recommenced with a spare pair for 100 strokes, followed by the eight pairs for 50 strokes each, and the spare pair for 100 strokes. This process was carried out eight times, and at the end of each run, the position of the second white line was reached almost exactly, and in no case was it more than one-sixteenth of an inch out of position.

In Table 12 the figures denote losses in grams for 100 strokes, obtained by adding the losses for 50 strokes of the left and right hand specimens of each pair.

The total of each column is the total loss in grams for 800 strokes, for each time the abrasive has been used. From these totals can be calculated the losses for 1000 strokes, and these are averages for the 8 pairs of specimens in each column. In Graph 6 (Figure 5) the losses for 1000 strokes are plotted against the number of times the abrasive was used, and it shows an appreciable decrease for the first and second times of usage. Thereafter the decrease is smaller, and approximately exponential as far as the eighth time. Taking the density of this rubber sheet as 1.31 g. per cc., the rate of 6.49 g. per 800 strokes, or 8.1 g. per 1000 strokes, is equivalent to 9.6 mm. per 1000 strokes.

The sum of any row is the total loss for a particular portion of the abrasive cloth, and the variance of row totals is 0.005014, based on 7 degrees of freedom. Let the portion of a rubber specimen removed by 100 strokes be called for brevity one layer. During this test each of the eight portions of the abrasive is used to abrade one layer from each of the eight specimens; moreover, if it is

TABLE 12  
TEST G. GRAMS PER 100 STROKES

Position on cloth	No. of times the abrasive has been used								Total
	1	2	3	4	5	6	7	8	
1	0.7919	0.7198	0.6924	0.6366	0.5873	0.5615	0.5430	0.5296	5.0621
2	0.8070	0.7124	0.6361	0.6090	0.5956	0.5613	0.5452	0.5412	5.0078
3	0.8152	0.7414	0.6627	0.6186	0.5845	0.5776	0.5340	0.5180	5.0520
4	0.8234	0.6961	0.6822	0.6072	0.5991	0.5547	0.5356	0.5276	5.0259
5	0.8274	0.7331	0.6478	0.6093	0.5721	0.5354	0.5237	0.5240	4.9728
6	0.7849	0.7095	0.6390	0.6591	0.6231	0.5435	0.5136	0.4812	4.9539
7	0.8260	0.7430	0.6871	0.6219	0.6225	0.5868	0.5615	0.5327	5.1815
8	0.8181	0.7341	0.6729	0.6174	0.5577	0.5599	0.5287	0.5083	4.9971
	6.4939	5.7894	5.3202	4.9791	4.7419	4.4807	4.2853	4.1626	40.2531

used to remove the outer layer of one specimen, it is used to remove the next layer of another, the third layer of another specimen and so on. In consequence of this, it must be true that each of the eight portions of the abrasive has had nearly the same opportunity of abrading, even if the rubber varies slightly in resistance to abrasion from specimen to specimen or from layer to layer, and it is reasonable to assume that the variance quoted is that of the cloth alone. This variance, therefore, is that between lengths of cloth used for 100 successive strokes. It is, however, that of the sums of eight trials on each length of abrasive, and the corresponding variance between the lengths used

for the 250 strokes of routine testing is  $0.005014 \times \frac{250}{800}$ , i.e., 0.001567. The mean loss of this rubber is 1.572 g. for 250 strokes. Hence, the contribution which the variability of the abrasive makes to coefficient of variation:

$$\left( 100 \times \frac{\text{standard deviation}}{\text{mean}} \right) \text{ is } 100 \frac{\sqrt{0.001567}}{1.572} = 2.52 \text{ per cent}$$

Let  $v_c$  be the variance between the eight different portions of the abrasive cloth used in the experiment, and  $v_r$  the variance of the corresponding layers of the rubber. Using the row totals,  $v_c$  is found to be  $\frac{0.005014}{8} = 0.000627$ , estimated on seven degrees of freedom. The data of each column provide the means of estimating the variance of rubber and cloth combined (i.e.,  $v_c + v_r$ )

and the value so obtained is 0.000348, based on seven degrees of freedom from each column, or fifty-six in all. The difference of the two variances is not significant, and as the estimate of  $v_c + v$  is less than the estimate of  $v_c$  alone, there is no evidence that  $v_r$  is appreciable in comparison with  $v_c$ . It seems likely that the variability of neighboring specimens from a sheet of rubber is small in comparison with that between the portions of the abrasive cloth used to test them, and this would explain the findings of test B. Most of the discrepancies of different abrasion results is to be attributed to slight lack of uniformity of the abrasive cloth.

The experiment is not sufficiently accurate, however, to demonstrate that the variability of the rubber is negligible.

*Acknowledgment.*—The author wishes to thank the Director and Council of the Boot Trade Research Association for permission to publish this paper, and also C. J. W. Gregory for help in the experimental work.

Total  
5.0621  
5.0078  
5.0520  
5.0259  
4.9728  
4.9539  
5.1815  
4.9971  
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## STUDY OF THE H TEST FOR EVALUATING THE ADHESIVE PROPERTIES OF TIRE CORD IN NATURAL AND GR-S RUBBERS \*

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The adhesion of cotton tire cord to natural rubber apparently never presented any special problem to the tire industry, supposedly because of the strong mechanical bond formed by the numerous loose or projecting cotton fiber ends which become embedded in the soft rubber during vulcanization. These fiber ends are not present in tire cords made from synthetic, continuous filaments; as a result of which there is poor adhesion of such filaments to rubber. With the production of GR-S, its adhesion to cotton tire cords was found to be inferior to that obtained with natural rubber, especially at higher temperatures. Often separation would occur between cord fabric and rubber immediately after the tires came from the vulcanizing molds and before they had cooled. It was obvious that special attention would have to be given to this problem.

The first step in the study of adhesion seemed to be the selection or development of a suitable test method for this property. The only published method that could be found—that given in A.S.T.M. Designation D413-39—involves the use of sections of finished tires, or fabric cured in rubber slabs, and is obviously both inconvenient and expensive. There were also other methods in use by The B. F. Goodrich Co., and the so-called H adhesion test originated by the Goodyear Tire & Rubber Co. The latter method was selected for use in this study because of its more general use in a number of laboratories and its previous application to cotton tire cord.

Essentially the H test is a measurement of the force required to pull a single cord, in the direction of its axis, from a strip of rubber in which one end of the cord over a given length is embedded. Thus the quantity measured is a shearing force acting across the cord-to-rubber surface. The opposite end of the piece of cord is held in the pulling clamp by lateral pressure from the jaws, transmitted through a second rubber strip. The two endstrips with the interconnecting cord form a specimen resembling the letter H, from which the test derives its name. The H-shaped specimens are obtained by cutting them from a cast, molded for this purpose, and consisting of a number of rubber strips interconnected at intervals by cords which extend through all the strips. The diagram of a typical mold in Figure 1 suggests the general form of the cast.

A visit paid to various commercial laboratories employing this test revealed that the technique was by no means standardized, e.g., forming molds of widely different sizes and thicknesses were being used. In addition other particulars such as type of rubber stock, curing cycles, test clamps, and other factors differed. Results from different laboratories could not, therefore, be compared, and selection of test conditions was necessary. This paper presents an

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experimental basis for the selections made, together with an outline of the proposed procedure.

## EQUIPMENT AND MATERIALS

### MOLDS, PRESS, AND TESTING EQUIPMENT

Two different molds were available for experimental use. Most of the test-specimens were made on a mold constructed from specifications furnished by the Armstrong Tire & Rubber Co., which will hereinafter be referred to as the Armstrong mold. The number and arrangement of the cord slots and rubber channels are shown in Figure 1. The plate is  $5\frac{1}{2}$  by 10 by  $\frac{5}{8}$  inches. The rubber strip channels are  $\frac{3}{8}$ -inch wide by 0.100-inch deep, and are separated from one another by  $\frac{1}{4}$ -inch. The ten cord slots are 0.040-inch wide by 0.100-inch deep, displaced from each other by one inch on centers.

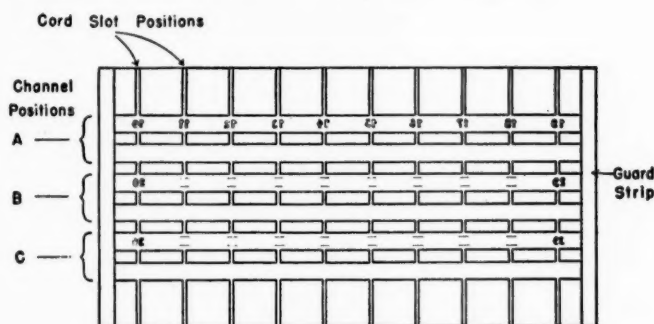


FIG. 1.—Armstrong Mold for "H" Adhesion Test

A second mold was constructed from specifications furnished by the Mansfield Tire & Rubber Co. and will hereinafter be referred to as the Mansfield mold. This mold was 12 by 14 by  $3\frac{1}{4}$ -inches. The pattern of rubber channels and cord slots in this mold is essentially the same as in the Armstrong mold, except that the channels are 0.125-inch deep and only 8 inches long.

A hydraulic press having steam-heated plates was used for curing in most of the experiments. Unless otherwise specified, the cure was for 30 minutes at 287° F in a previously heated mold, under a pressure of 550 lbs. per sq. in. on the mold face. The casting was then removed and allowed to stand for a period of time, usually 24 hours or more. The casting was then cut so as to give one test-specimen for each cord position and set of channel positions shown in Figure 1.

The adhesion of cord to rubber was measured in most cases with a Scott tester; the capacity was set at 50 pounds. In a few cases, a Suter tire-cord tester with autographic recorder was used; the capacity was set at 25 pounds. The jaw speed was four inches a minute in a number of the earlier tests and then 12 inches a minute, unless otherwise noted. Special clamps were constructed patterned after those in use by the Mansfield and Armstrong laboratories.

Since the study was also to determine how cord-to-rubber adhesion varies with temperature, usually half the specimens from each casting were tested at elevated temperature; 275° F was used unless otherwise noted.

## RUBBER STOCKS

Five different tire carcass stocks were used in the study. The sample numbers, types of rubber, dates of receipt, and molds for which intended were as follows:

Sample no.	Type of rubber	Date of receipt	Mold
Co-767	Natural	Sept. 10, 1943	Armstrong
Co-768	GR-S, S-4	Sept. 13, 1943	Mansfield
Co-783	GR-S, S-4	Sept. 21, 1943	Armstrong
Co-1063	GR-S, S-4	Nov. 20, 1943	Armstrong
Co-1352	GR-S, S-4	Feb. 29, 1944	Armstrong

The Armstrong mold stocks were sheeted, rolled on to frictioned, square-woven backing cloth to give a gauge of about 0.055 inch, and then covered with Holland cloth. The Mansfield stock was sheeted to a gauge of approximately 0.070 inch and then rolled on to a plain unfriictioned duck to give an over-all gauge of 0.105 inch. The other surface was covered with Holland cloth.

## TIRE CORDS

For most of the tests two different tire cords, both manufactured from the same Stoneville 2B cotton, were used. One cord, designated Co-752, was of 24/4/3 construction, had a cable twist of 10.5 turns per inch, a gauge of about 0.0285 inch, and was referred to as "low gauge." The other cord, designated Co-753, was of 23/5/3 construction, had a cable twist of 8.7 turns per inch, a gauge of about 0.0315 inch, and was referred to as "medium gauge".

## INFLUENCE OF EXPERIMENTAL CONDITIONS ON OBSERVATIONS

## PREDRYING OF THE CORD

Two series of tests were made, from which it was concluded that the drying of untreated cotton tire cord before use in the adhesion test could, under ordinary circumstances, be safely dispensed with. In the case of treated tire cord, the influence of moisture on the adhesive itself would naturally dictate the procedure to be followed.

## PRESSURE ON MOLD DURING CURE

Two experiments were conducted to determine the influence of mold pressure. These tests were made with different rubber stocks and tire cords. The results indicate that pressure during curing has no significant influence on the results of cold measurements, but suggest that it does influence the results when the adhesion is measured hot. This latter difference is associated only with low pressures, and is not appreciable in the 290-542 lbs. per sq. in. pressure range. In routine work it would seem advisable to use a curing pressure similar to that used in tire manufacture, i.e., 250 lbs per sq. in.

## TEMPERATURE

To obtain information on the behavior of cord-to-rubber adhesion as a function of temperature, a series of tests employing four different rubber stocks, medium-gauge cord Co-753, and covering a temperature range from 77-300° F, was undertaken. The results are shown graphically in Figure 2. Adhesion of the cord at room temperature (77° F) and again at about 275° F was the

same for all four stocks. Between these points natural rubber exhibited the best adhesion, but its adhesion fell off more rapidly above 275° F than did that of the synthetic stocks. The temperature of 275° F appears the highest to which adhesion specimens can be exposed without severe damage to adhesive properties, and is recommended as a routine temperature for use in high-temperature adhesion tests. Additional tests revealed poor correlation between adhesion test results at room and high temperatures, showing the need of "hot" adhesion measurements as a routine part of the testing procedure.

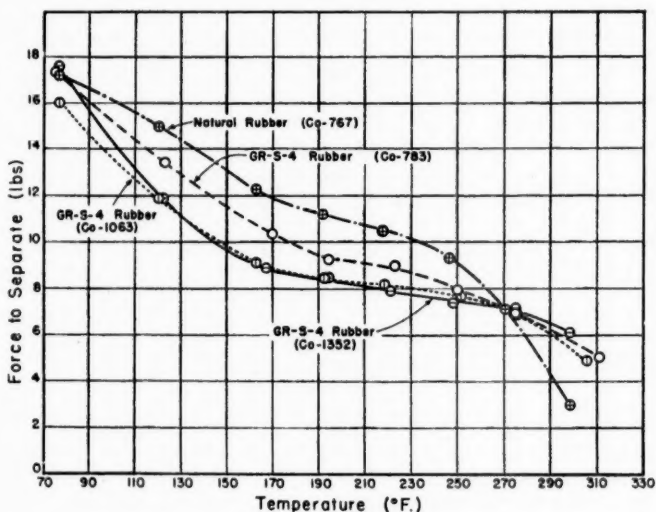


Fig. 2.—Adhesion of Various Rubber Stocks to Cotton Tire Cord at Different Temperatures

#### SPEED OF PULLING CLAMP

Tests were made which clearly showed adhesion values to increase progressively with increasing clamp speed, both at room and elevated temperatures. A speed of 12 inches per minute is recommended for the moving clamp for the following reasons: to increase magnitude of reading and decrease effect of frictional losses; to conform with conventional clamp speeds; and to secure the highest possible rate of loading of the cord itself.

#### POSITION OF TEST-PIECE IN THE CURING MOLD

Investigation showed a significant difference in adhesion associated with channel positions in the mold, but none associated with cord positions. Analysis of test procedure and results, however, gave the conclusion that any source of influence of channel positions on adhesion must have been exterior to the mold. Nevertheless in tests recorded here it was the practice, in any one test, to lay the series of test cords in the cord slots in a progressive succession in such a way that each cord sample occupied as many different cord slots in the different cures as possible.

## CHARACTER OF JAW SURFACES AND PRESSURE ON CLAMPS

Tests were conducted to check the belief that adhesion measurements in the H test were very sensitive to the conditions under which specimens were attached to clamp jaws in the tester. From the results it appears that any corrugations put into the rubber support strip of the test specimen by the serrated jaw surfaces are not communicated across the jaw slit to the embedded cord and do not, therefore, affect adhesion measurements. Additional experiments also showed that differences in clamping pressure of the jaws are not reflected in adhesion measurements.

## CALENDERING-DIRECTION IN RUBBER CHANNEL STRIPS

Experiments were made to determine effect of mechanical anisotropy of rubber from calendering operations, and possible effect of directions of warp and filler of the backing cloth with respect to direction of specimens. The results indicate definitely that the orientation brought about in the test specimen by calendering has no influence on adhesion values. This is also the case for differences in direction of backing cloth yarns and test-specimens.

## DIFFERENCES IN MOLDS

Tests were made with different stocks in both the Mansfield and Armstrong molds, using 250 lbs. per sq. in. as curing pressure on the mold face in all cases. Analyses of the results indicate that the use of different molds, stocks, and cures gave highly significant differences in adhesion values.

## PRESENCE OF CENTRAL RUBBER SHEATH AROUND CORD

It was thought that the rubber sheath which forms around the cord between the two rubber strips during molding might affect adhesion measurements. Experiments conducted to determine this effect indicate that the sheath causes increases in adhesion values at both room and high temperatures. The increases were about the same at both temperatures and, in some cases, exceeded 25 per cent of the total. Since the sheath affects the absolute magnitude of the adhesion force, corrections for this effect are not necessary in evaluating testing techniques, rubber stocks, etc., where the effect may be considered to be the same in all samples tested. The method for treating this correction is described in a later section on characteristic adhesion.

## INFLUENCE OF TIME AS A FACTOR IN THE TEST

## PERIOD OF TIME ELAPSING BETWEEN CURING AND TESTING

Tests were made to determine whether the 24-hour aging period customarily used is significant. The results show that adhesion does increase for a time after curing, at least when measured at room temperature, but that it comes to a stable value during the first 24 hours, after which there is no appreciable change. On the other hand the experiments indicate that no upper limit need be placed on the period between curing and testing. Even if tests at 275° F failed to show any effects of delayed testing on adhesion, the use of a 24-hour waiting period appears desirable for uniformity.

## LENGTH OF HEATING PERIOD FOR SPECIMENS AT 275° F

The adhesive forces of specimens tested immediately after removal from the oven show a slight drop between one- and 1½-hour heating periods, indicat-



ing that the specimens do not quite reach the prevailing oven temperature after only one hour of heating. Variations in adhesion for specimens heated for  $1\frac{1}{2}$  hours or longer are not significant, justifying the decision that  $1\frac{1}{2}$  hours is the optimum heating period for the test at 275° F.

#### DELAY IN TESTING HOT SPECIMENS

The time delay in testing hot specimens can conceivably affect adhesion measurements in high-temperature tests. Experiments to check this factor indicate that a delay in testing up to about one minute introduces no significant difference (error) in high-temperature adhesion tests. For longer delay periods the observed adhesion forces rise. After 90 minutes the specimens regain about 85 per cent of the loss in adhesion due to high temperature.

#### RUBBER-STOCK FACTORS INFLUENCING ADHESION

##### DIFFERENCES BETWEEN RUBBER STOCKS

Differences in adhesive behavior between the natural and GR-S rubber samples, and between the three GR-S samples themselves, are shown in Figure 2. It was to be expected that the adhesion of tire cord would be different for the various types of rubbers, for rubber of the same type but from different sources, and for batches compounded at different times.

##### TIME AND TEMPERATURE OF STORAGE OF GR-S STOCK

Tests reveal that stocks stored at 45° F in a refrigerator show neither a gain nor an appreciable loss in adhesion whether measured at room or at elevated temperatures. Although the adhesion measured at room temperature declines steadily if the stock is stored for long periods at room temperature before curing, the adhesive force measured at 275° F appears not to be affected. It is, therefore, evident that storage of uncured stock at a low temperature is necessary to obtain reproductive results.

##### UNIFORMITY OF ADHESION WITHIN A SINGLE ROLL OF GR-S STOCK

It was determined that samples of a stock, Co-1352 in this case, were substantially uniform throughout the length of the roll, insofar as its adhesive properties were concerned.

#### CORD FACTORS INFLUENCING ADHESION

##### GAUGE OF CORD

Account must be taken of the gauge in assessing the merits of different factors that influence adhesion, when cords of different gauge are employed. Results of experiments conducted show that increase of gauge results in a progressive increase in adhesive force. The observed data are in reasonable agreement with values computed from the equation:  $A = k\pi GL$ , where  $A$  is the measured force of adhesion,  $G$  is the measured gauge of the cord (here used as diameter),  $L$  is the contact length, and  $k$ , the proportionality factor, is the adhesive force per unit area. The data obtained in tests of gauge effect on adhesion are plotted in Figure 3. It is evident that whenever the adhesion of cords of different gauge is to be compared, adjustment must be made for differences in gauge. The method for making this adjustment is discussed in a later section on characteristic adhesion.



## NUMBER OF PLYS AND CORD TWIST

Tests were made on two and three-ply cords having the same number of turns per inch, and on cords of the same ply having a range of twist. In general the two-ply cord and 3-ply cord showed no significant difference in adhesion, but a slight increase in adhesion was noted with increasing twist.

## ADJUSTMENT FOR CORD TWIST

A relation whereby the adhesion of a cord having a given twist could be calculated from observations on a similar cord having some other twist would be useful in many cases. While the evidence to which reference has been made

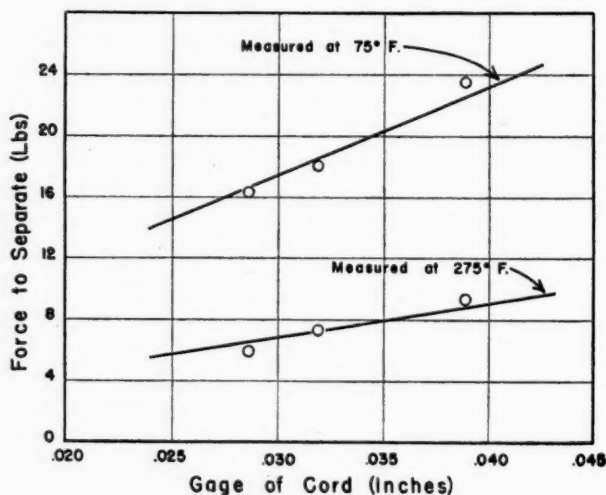


FIG. 3.—Effect of Gauge on Rubber-Cord Adhesion

in the foregoing section favors cord angle rather than turns per inch for adjustment of different constructions, the former is less convenient in practice. Since the effect is very small, adjustments may be made in characteristic adhesion with sufficient accuracy by means of the following derived equation involving the turns per inch:

$$K_2 = K_1 + 13.7(T_2 - T_1)$$

where  $K_1$  and  $K_2$  are the available and desired characteristic adhesion, respectively, and  $T_1$  and  $T_2$  are the corresponding turns per inch in the cord. For the characteristic adhesion measured at 275° F, substitute 5.6 for the value of 13.7 in the equation above. From these equations the average increase in adhesion is only 13.7 lbs. per sq. in. per turn per inch at room temperature, and 5.6 lbs. per sq. in. per turn per inch at 275° F.

## THE CHARACTERISTIC ADHESION

## DEFINITION

In the section of gauge of cord it was pointed out that adhesion varies with the gauge of the cord and can be traced to variation of the area of adhesive

surface with gauge. When the measured adhesion is expressed as a ratio of the cord surface involved, the significant effect of gauge disappears. By transposing the terms of the equation given in that section, we obtain:

$$\frac{A}{G} = k\pi L$$

where the left-hand term characterizes the adhesion, in shear, of a particular cord, independently of the gauge. Since evidently the ratio  $A/G$  is proportional to  $L$ , we may refer the ratio to unit length of contact (one inch) by dividing by  $L$ :

$$\frac{A}{GL} = k\pi = K$$

Insofar as the observed value,  $A$ , gives the force actually required only to shear the cord-rubber bond of one cord along the length  $L$ , the quantity  $k\pi = K$  measures the adhesion of a particular cord-rubber combination independently of gauge and length of contact. It may be interpreted physically, in the ideal case, as the force required to shear a one-inch width of tightly packed cord fabric from a one-inch square of rubber. Since the length of contact of cord to rubber, after removal of the rubber sheath around the cord between the end-strips, is always  $\frac{1}{2}$ -inch in the present H test, we have:

$$K = \frac{8A}{3G}$$

where  $A$  and  $G$  are the measured adhesion in pounds, and cord length in inches, respectively.  $K$  may be called the *characteristic adhesion*.

#### ESTIMATION OF CHARACTERISTIC ADHESION FROM TESTS ON SPECIMENS WITH SHEATH PRESENT

In some cases the procedure followed may not involve removal of the sheath. Data are presented in Figures 4 and 5 from tests attempting to correlate characteristics adhesion with crude characteristic adhesion (computed for the specimens with sheath present). Reference to these figures shows that a definite correlation does exist. The regression equations, computed by the method of least squares and assuming a linear relation, for characteristic adhesion are:

$$\begin{array}{ll} \text{At } 75^\circ \text{ F:} & K = 0.8960 K_u + 5395 G - 299 \\ \text{At } 275^\circ \text{ F:} & K = 0.5518 K_u + 3305 G + 65 \end{array}$$

where  $K_u$  is the crude characteristic adhesion, and the gauge,  $G$ , is expressed in inches. Further analysis of the data showed that the correlation coefficient associated with the equation at  $75^\circ \text{ F}$  was 0.934 and the standard error of estimate 70.3 lbs. per sq. in. For the equation at  $275^\circ \text{ F}$ , the respective figures were 0.760 and 58.6 lbs. per sq. in. Regression lines corresponding to the gauges 0.024-inch and 0.032-inch are drawn in Figures 4 and 5.

#### PROPOSED PROCEDURE FOR CONDUCTING THE H ADHESION TEST

##### RUBBER STOCK AND PREPARATION OF MOLDED TEST-SPECIMENS

The rubber skim stock, both natural and synthetic, cut into sections of 10 by 12 inches, is stored at low temperature, preferably in a refrigerator.

Before use each new supply is gauged with a dial micrometer to make certain that cut pieces will completely fill the mold channels and make possible some overflow during curing. The Holland cloth is not included in this gauge. Skim stock with backing fabric for use in the Armstrong mold should have a gauge of about 0.055 inch, but not below 0.050 inch. The skim stock with backing fabric for use in the Mansfield mold should have a gauge of about

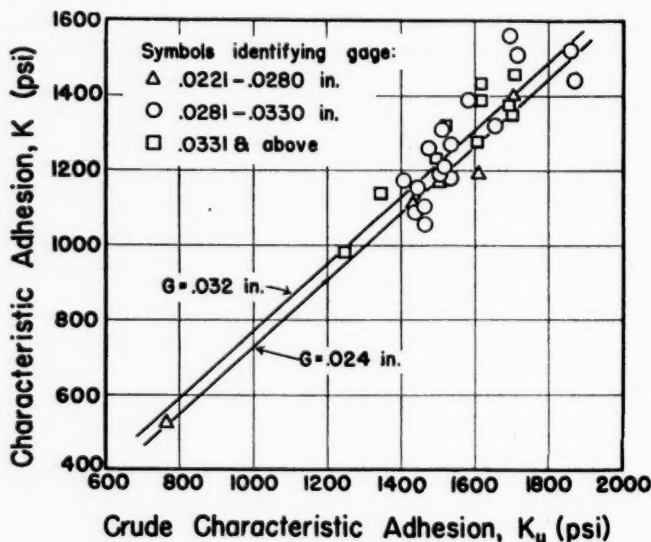


FIG. 4.—Characteristic Adhesion as a Function of the Crude Characteristic Adhesion (Sheath Present), Determined at 75° F.

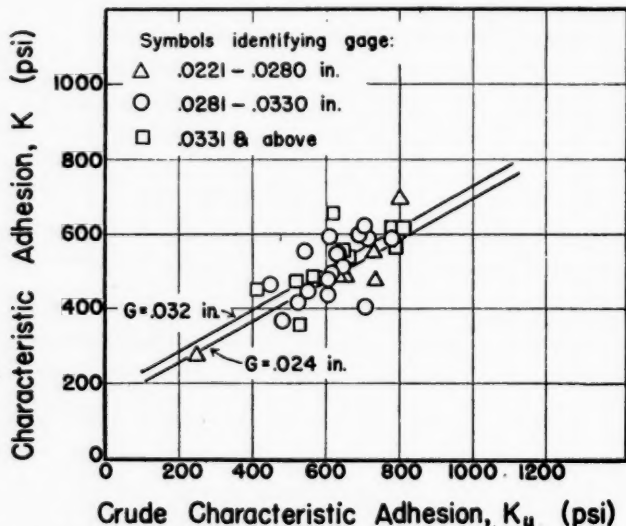


FIG. 5.—Characteristic Adhesion as a Function of the Crude Characteristic Adhesion (Sheath Present), Determined at 275° F.

0.095 inch, including canvas. The mold with cover, previous to curing, is placed between the hot plates of the hydraulic press and allowed to heat up with the plates as steam passes through the latter.

With a cutting tool in which the blades are spaced to match the mold channel width, strips of skim stock are cut 10 inches long for the Armstrong mold, or eight inches long for the Mansfield mold, with the length of the strips parallel to the warp of the fabric. Before the molding operation, the gauges of the cord samples being tested are to be obtained. Cords are to be in a normal condition of humidity, and specimens should be about 10 inches long for the Armstrong mold, and 16 to 18 inches long for the Mansfield mold. Before being cut to length, the cord should be knotted about  $\frac{1}{2}$ -inch from the end of each specimen to avoid loss of twist during handling. In addition to test cords, the use of an identical cord as a control is advantageous.

When the press and mold have been at the required temperature of 287° F for about 15 minutes, the mold is removed to a table. The rubber strips are pulled one by one from the Holland cloth and quickly fitted, with fabric side down, into the six channels in the mold. The cord specimens, properly identified, are now laid in the transverse cord slots in the mold so as to cross the skim coat of the rubber strips. Each cord is held in place by the end knot resting against the back edge of the mold, and a four-ounce weight is clipped to the other end of the cord hanging down over the edge of the mold to provide uniform tension.

When all the cords are in place, the remaining six strips of rubber are pulled from the Holland cloth, laid in the channels, with the skim coat down, directly over the strips already in the mold, and pressed into place to avoid overlying the channel edges at any point. The cover is replaced on the mold; the weights are removed from the cords; the protruding ends of cords are clipped off near the edge of the mold, and the assembly is placed into the press, all as quickly as possible. The rubber is cured for 30 minutes at 287° F (or at the proper temperature for the stock) under a load computed to give a pressure of 250 lbs. per sq. in. on the mold surface. When curing is complete, the rubber casting is set aside for at least 24 hours before testing.

#### SEPARATION OF SPECIMENS AND MEASUREMENT OF ADHESION

The specimens cut from the casting are divided into two parts: one for adhesion tests at room temperature, the other for tests at elevated temperatures. Before testing, the rubber sheath around the cord and the flash between rubber end-strips are removed without disturbing the rubber about the cord entering the strip.

All adhesion tests are made on a vertical pendulum-type rubber or textile testing machine, with the speed of the moving clamp to be fixed at 12 inches per minute. The upper clamp is to have a continuous clamping surface across the whole width of each jaw. The lower clamp fits on a stud on an adapter through which the breaking force is applied. This clamp has a vertical slot about  $\frac{3}{16}$ -inch wide in the middle of both jaws. For tests at elevated temperatures, specimens are mounted in individual lower clamps, and the assemblies heated to the proper temperature and kept in the oven until ready to test.

#### ADJUSTMENT OF RESULTS TO A BASIC CONTROL

The use of a basic control cord sample is especially valuable in disclosing variation introduced into the results by a new technician, or the use of a differ-

ent testing machine, or any other of a number of sources of error. After a number of separate tests have been run, each containing the basic control cord, an average value is calculated for the characteristic adhesion,  $K$ , of the control cord. In comparing results from different tests, then, the  $K$  values for all the samples in a given test are first adjusted by the ratio of the  $K$  of the control cord in that test to the mean of the  $K$  values for all tests, as:

$$\text{Adjusted } K = \text{Original } K \times \frac{\text{Average } K \text{ for basic control}}{K \text{ for basic control of given test}}$$

A control chart may be kept of the characteristic adhesion over the period of testing. Such a chart appears in Figure 6, where the different symbols represent the rubber stocks used. The solid line represents the grand average

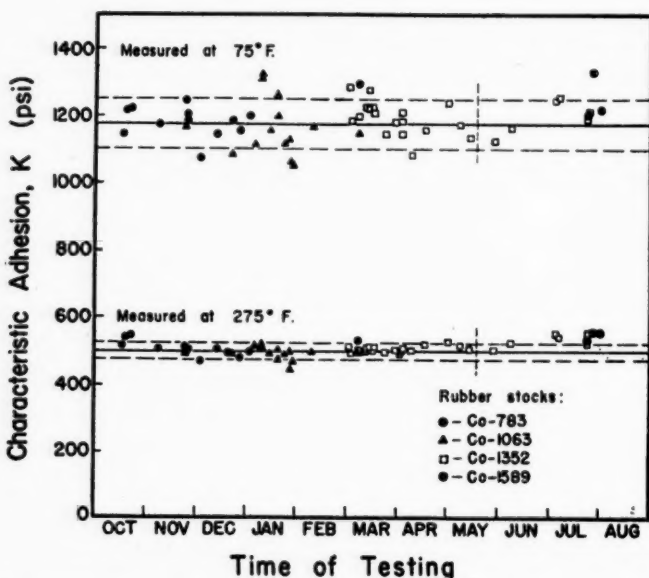


FIG. 6.—Control Chart for Judging the Homogeneity of Characteristic-Adhesion Means Obtained on the Basic Control Cord. The Central Lines and Control Limits Were Computed from the Data of 41 Tests Made during the First Eight Months, Indicated by the Vertical Dashed Lines.

characteristic adhesion of the control cord, obtained in forty-one tests during the first eight months shown. The dashed lines represent the control limits, calculated from the standard errors of the individual test means according to the procedure recommended by A.S.T.M. Committee E-1 on Methods of Testing in its manual on presentation of data. The limits can, of course, be chosen to meet the particular situation. Then, an increase in variance of data due to change in stock or other condition affecting the basic control is made evident by the new values falling outside the control limits more than the expected proportionate number of times. It may be noted from the chart that values for the last two months, July and August, do not follow the same trend as earlier values, owing to the use of a new testing machine whose calibration evidently does not agree with that of the old machine.

## EXAMPLES OF APPLICATION OF THE METHOD

The application under the proposed conditions of the H adhesion test to a series of typical cotton and rayon tire cords is shown in Table 1. It will be seen that rayon cord without treatment has a very low characteristic adhesion, when compared with cotton cord, but that the adhesion at both normal and high temperatures is nearly up to cotton after treatment with a commercial adhesive. The characteristic adhesion of nylon is seen to be somewhat better than that of rayon, but still far below that of cotton.

TABLE 1  
APPLICATION OF "H" ADHESION METHOD TO VARIOUS TIRE CORDS

			Characteristic adhesion*			
			At 75° F		At 75° F	
Sample no.	Tire cord and treatment	Cord gage in.	Absolute lbs. per sq. in.†	Relative %	Absolute lbs. per sq. in.	Relative %
Co-973	Rayon cord, untreated, 1100/2	0.0240	275	100	188	100
Co-1157	Rayon cord, treated commercial adhesive	.0255	969	352	435	231
Co-971	Nylon cord 210/4/2	.0160	307	..	212	..
Co-893	Rayon cord, untreated	.0224	235	..	162	..
Co-968	Cotton cord, Standard 16/4/3	.0342	1119	..	471	..
Co-753	Cotton cord, GR-S Stock Co-783	.0315	1175	100	499	100
Co-753	Cotton cord, initial test of new GR-S Stock Co-1063	.0315	1077	92	496	99
Co-753	Untreated	.0315	1175	100	499	100
Co-1233	Co-753 extracted ethyl acetate	.0325	1226	104	498	100
Co-1234	Co-753 extracted acetone	.0314	1211	103	509	102
Co-996	Co-753 extracted benzene	.0330	1176	100	515	103
Co-1444	Co-753 extracted xylene	.0288	1130	96	433	87
Co-1061	Co-753 with commercial adhesive	.0364	†	†	633	127
Co-1232	Co-753 with polyvinyl acetate	.0337	710	60	354	71

\* Adjusted to mean of basic control cord.

† Based on untreated cord.

‡ Cord broke before separation occurred.

## PRECISION OF THE METHOD

Since a basic control cord was included in all the tests, the results make it possible to calculate the standard error. The observed standard error in characteristic adhesion at 75° F, based on forty-one different tests, is 4.9 per cent, and the computed error from within-test variation is 2.6 per cent. The respective errors at 275° F are 5.9 and 3.2 per cent. This analysis therefore shows the presence of further still unidentified and uncontrolled variables.

## SUMMARY

The H adhesion test has been adopted tentatively for evaluating the adhesive properties of cotton and other tire cords in natural and GR-S rubber. The various factors which could be expected to influence the adhesion or its measurement fall into four broad classes: experimental conditions, time factors, rubber-stock factors, and cord fabrics.

Predrying of cotton cord and variations in the pressure on the mold have no significant effect on adhesion. The temperature of test is highly important. Among the factors involved during molding of specimens, direction of calendering of the rubber stock and differences in types of molds used have, in general, little or no influence. The position of the specimen in the mold is likewise not of importance. The rubber sheath around the cord between the end strips



of each specimen causes significant, but spurious increases in adhesion. As regards the testing machine, the conditions of clamping of the specimen are without effect, but the speed of the pulling clamp makes significant variations in adhesion.

A 24-hour aging period is necessary for testing at room temperature, and a 1½-hour heating period is needed before testing of specimens at high temperatures. A one-minute delay in testing of high temperature specimens has no effect. Storage of uncured rubber stock at low temperatures (approximately 45° F) before building test-pads is important.

The force required to separate a cord from rubber increases linearly with the gauge and requires adjustment when comparing tests of cords having different gauges. The characteristic adhesion is defined and shown to give a practical estimate of adhesion. The twist of a cord has a small influence on the adhesion, and adjustment formulas are given to make possible the comparison of cords having different twists.

A description is given of a recommended procedure for conducting the H adhesion test. The proposed method, based on the findings of this study, aims to provide means for evaluating or holding uniform those factors which have significant effects on the results. Data accumulated during the study reveal that the standard error in the characteristic adhesion obtained by use of the proposed method may be expected to be about 5 per cent at normal room temperature and about 6 per cent at 275° F.

## TEAR RESISTANCE

### More Accurate Results Using I.C.I. Tear Cutter \*

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#### INTRODUCTION

In a previous publication<sup>1</sup> attention was drawn to the fact that when carrying out tear resistance tests according to A.S.T.M. D.624-44, great care must be exercised when preparing the samples. Crescent shaped samples are used, a nick 0.02 inch in depth is introduced in the center of the crescent, and the force required to tear across the unnicked portion is measured. The I.C.I. method of nicking the samples was described in the previous paper. A new and improved method has since been developed, and is described in the present paper. It was shown<sup>1</sup> that the tear resistance of vulcanized rubber is very susceptible to the depth of the initial nick. This is illustrated in Figure 1.

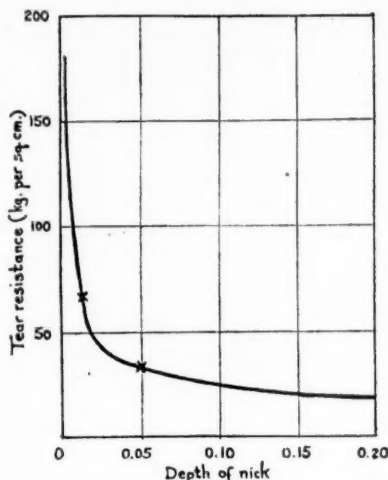


FIG. 1.

Effect of depth of nick on the resistance to tearing of a natural rubber vulcanizate.

With an initial nick of 0.02 inch, very small variations in the depth can produce quite wide differences in the tear resistance values. With most rubber compounds the 0.02-inch nick is in the region AB, where the slope of the graph is changing most rapidly (see Figure 1).

Therefore, when testing tear resistance according to A.S.T.M. 624-44, it is essential that the nick be accurately introduced. The A.S.T.M. do not specify

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a tolerance value for the depth of nick, an omission which should be rectified at the earliest opportunity.

### DESCRIPTION OF NEW CUTTER

The crescent-shaped test-piece (1) is clamped in carriage (2), which is mounted so that it can slide in V-shaped guide rails (3). A razor blade (4) is held in the robust clamp (5), which can move only in a vertical line. The razor blade enters slot (6) in carriage (2) and makes the required nick.

The test-piece (1) is held by clamp (7) under a constant load by the spring loaded discs (8), which swing clear of the clamp on the pins attaching them to the carriage. The carriage (2) is rebated to locate the test-piece, and the clamp

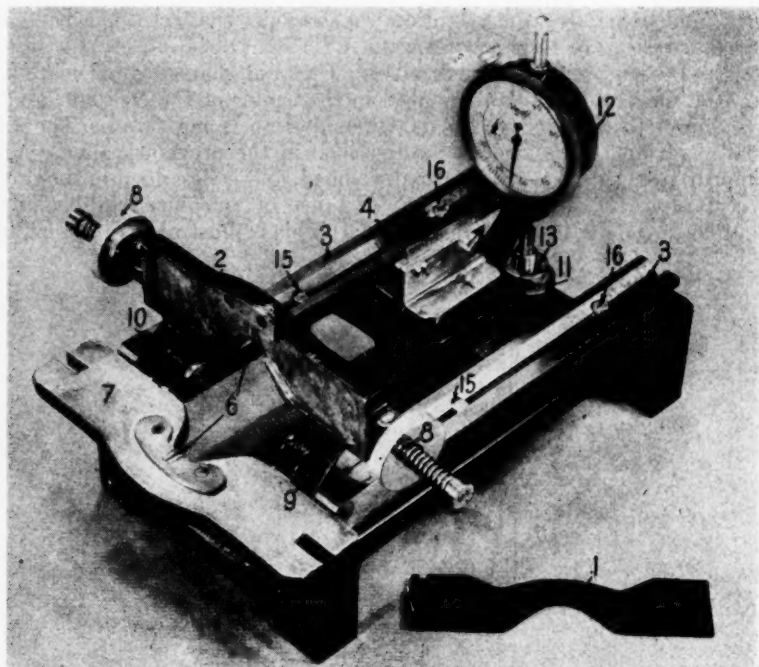


FIG. 2.

(7) is relieved so that the rubber in the region of the slit is firmly clamped. The clamp is loosely hinged at points (9) and (10) to the carriage. These hinges have a fine end clearance which assures the alignment of the slots in the carriage and the clamp.

The height of the razor blade is fixed by an adjustable stop (11), and is set by the dial micrometer (12), which reads in 1,000th inch. The position of the stop is fixed by tightening lock nut (13). A simple lever connects stop (11) with the razor blade clamp (5).

When the key (14) is depressed, the lever also actuates two moveable stops (15) on the V-guide rails, which, in conjunction with the fixed stops (16) in each rail, limit the movement of the carriage during the cutting stroke. Thus the

carriage with the test-piece cannot be brought into position for cutting without first lowering stops (15) by means of key (14), which also lowers the razor blade clamp. In this position, when set to give the standard 0.02 inch nick, the cutting edge of the razor blade is below the level of the edge of the crescent test piece, and the cutting operation cannot begin until key (14) is released.

The apparatus is illustrated in Figures 2 and 3.

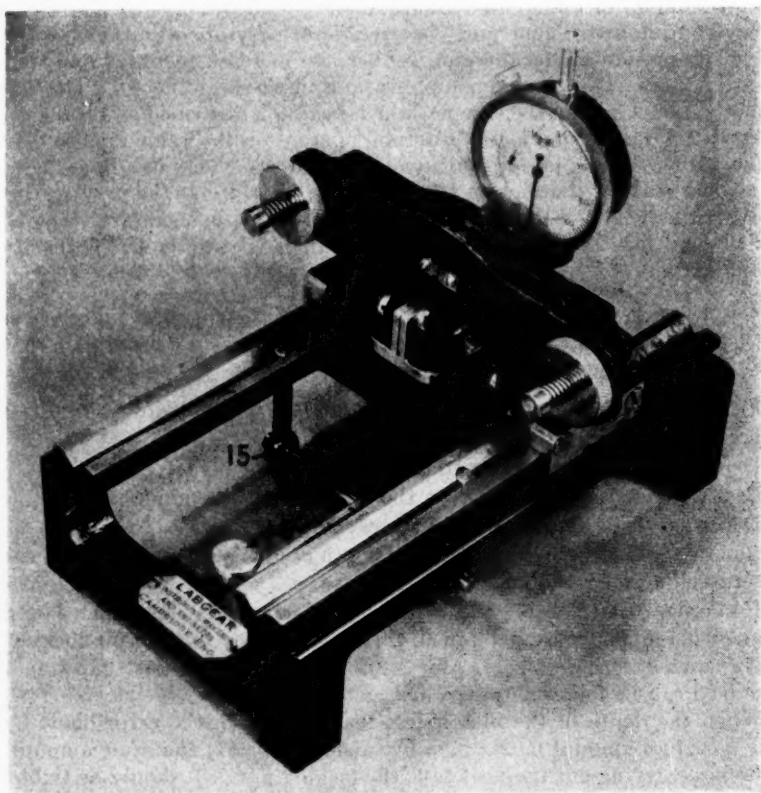


FIG. 3.

#### ADVANTAGES OF NEW CUTTER

The present instrument embodies several improvements over that described previously<sup>1</sup>. The razor-blade holder is accurately centered and no lateral movement of the razor blade is possible. Absolutely vertical nicks are thus assured, for lateral movement of the sample holder is also impossible because of the V-shaped guide rails.

The sample is clamped in the region where the nick is introduced, so deformation of the rubber in front of the cutting edge is reduced to a minimum. Previously it was extremely difficult to nick accurately gum stocks or soft unloaded compounds. Frequently a different setting of the razor blade holder was required to obtain a standard 0.02 inch nick with compounds of different hard-

ness, *e.g.*, gum and tread compounds. This difficulty has not always been appreciated and may explain some of the large variations which are normally associated with tear resistance results. The present method of clamping the sample seems to have overcome this difficulty and compounds of widely different hardness have been nicked successfully with a 0.02 inch nick at the same setting of the razor-blade holder. Undercured samples of Butyl rubber are notoriously difficult to cut or nick accurately, but it has been possible to prepare accurate samples of undercured Butyl rubbers with the present instrument.

Any routine instrument must be capable of easy operation, and when designing the present model the aim has been to increase accuracy and simplify the procedure. Three main simplifications have been made. The first is the method of clamping the sample, which has been described and is illustrated in Figure 2. The second is the provision of stops on the guide rails so that the sample holder can be passed quickly backwards and forwards over the razor blade when making the nick in the rubber. The third is the easy method of adjusting the height of the razor-blade holder. This is necessary when a new razor blade is fitted in the holder or when tear tests at different depths of nick are required.

#### METHOD OF NICKING THE SAMPLES

The following method is recommended:

- (1) Fit test-piece into recessed portion of carriage (2) and close clamp (7).
- (2) Brush the razor blade edge with soap solution.
- (3) Depress key 14 and slide carriage over the razor blade.
- (4) Pass carriage six times between the two stops in the guide rails.
- (5) Depress key 14 and draw back the carriage.
- (6) Remove test-piece and measure the depth of nick on both sides by means of a travelling microscope.
- (7) If the depth of nick is greater than 0.02 inch, say  $x$  inch, then lower the razor blade holder by  $x$ .02 inch. This is done by unscrewing locking nut (13) and lowering stop (11) by  $x$ .02 inch. The amount that stop 11 is moved can be followed on the dial gauge.

When the depth of the nick is less than 0.02 inch, the razor blade holder is raised an amount 0.02- $x$  inch by raising stop (11) the same amount.

Before carrying out the next test, the locking nut (13) should be tightened.

- (8) Another check test following operations 1-6 is carried out and a nick of 0.02 inch should be obtained.

#### ACCURACY OF THE INSTRUMENT

To check the accuracy of the instrument, tests were carried out with natural rubber and GR-S. The details of the compounds used are given below.

Natural rubber	100	GR-S	100
Zinc oxide	5	Zinc oxide	5
Stearic acid	3	Stearic acid	1
Kosmobile-HM	47.5	Kosmobile-HM	50
Sulfur	3	Pine tar	3
Vulcafor-MBT	0.85	Sulfur	2
		Vulcafor-F	1.6
Cure:	50/141° C		60/141° C

Twelve 2-mm. sheets of each mix were prepared and six test-pieces cut from each sheet, giving 72 test-pieces in all. The samples were nicked according to the method just described. The depth of nick of each sample was measured by means of a travelling microscope and the tear resistance measured on a Goodbrand tensile tester with a rate of separation of the lower jaw of 400 mm. per minute.

A statistical analysis of the results was carried out and the coefficients of variation<sup>2</sup> determined are given in Table 1.

TABLE 1

Rubber	% Coefficient of variation (depth of nick)	% Coefficient of variation (tear resistance)
Natural rubber	6.6	7.9
GR-S		11.0

The standard deviation in the depth of nick was 0.0013 and therefore  $\pm 2\sigma = \pm 0.0026$ . This means that, with the present instrument, a tolerance value of  $\pm 3$  thousandths inch can be specified. The coefficient of variation 7.9 per cent cannot be entirely due to variation in the depth of nick, for with tensile strength determinations coefficients of variation of the same order, *e.g.*, 7 to 10 per cent, have been reported<sup>3</sup>. For the present it will be considered satisfactory if we can reduce the variations in tear resistance tests to the same order as that obtained with tensile strength tests. Another factor which produces variations in tear resistance tests is the presence or absence of knotty tears. This subject has been dealt with previously<sup>1</sup>, and it is sufficient to note here that whereas straight tearing occurred in the majority of cases 20 examples (out of 72 samples) of knotty tearing were noted. Naturally the coefficient of variation is increased to an unknown extent by these samples. The coefficient of variation (11.0 per cent) in the tear resistance of the GR-S samples is greater than that of natural rubber, but it is well known that results of rupture tests are more variable with GR-S than with natural rubber. This is presumably due to greater variability in the raw GR-S. Meanwhile the improvement in GR-S results with the new cutter is considerable.

#### METHOD OF AVERAGING RESULTS

The A.S.T.M. method<sup>4</sup> of averaging tear resistance results is completely unsatisfactory. The whole question of averaging test results requires careful study, and work on this subject is in hand at Blackley.

The results of the present investigation have been averaged by the following five methods:

- (1) Mean.
- (2) Average of the four highest results.
- (3) Median.
- (4) Average of all results within 10 per cent of the highest results.
- (5) Average all results giving an average with 10 per cent of the highest result.

Frequency distributions of these five averages have been plotted to assess which method of averaging gives most information. As the subject will be dealt with fully in another paper, only a brief statement of the conclusions



arrived at will be given here. Either taking the median or the mean of the four highest results is to be preferred to the other three methods of averaging. There is little to choose between the median or the average of the four highest results. In the I.C.I. Rubber Service Department we have standardized on testing six samples and taking the median of the results.

#### METHOD OF EXPRESSING RESULTS

In a previous paper<sup>1</sup> detailed reasons were given why tear resistance results with the A.S.T.M. test-piece should be expressed in kg. per sq. cm. or lbs. per sq. in. and not in kg. per cm. or lbs. per in. As the width of the test-piece is 0.4 inch (1.016 cm.) there is practically no difference in the numerical value when expressed in kg. per sq. cm. but the order of the results is completely changed when expressed in lbs. per sq. in.

For example, when a force of 10 lbs. is required to tear a sample 0.09 inch thick, remembering that the effective width of the sample is 0.38 inch:

$$\text{Tear resistance} = \frac{10}{0.38 \times 0.09} = 293 \text{ lbs. per sq. in.}$$

When the width is not taken into consideration:

$$\text{Tear resistance} = \frac{10}{0.09} = 111.1 \text{ lbs. per in.}$$

#### ANGLE TEAR TEST

A case where the width of the specimen must be considered is in any comparison of tear resistance results using different test-pieces. When the first part of this investigation<sup>1</sup> was in the press, a new type of tear-specimen was suggested<sup>5</sup>. The angle-tear specimen, where the stress is concentrated by means of a 90° angle, has much to recommend it. As the angle and crescent test-pieces are of different width, the author<sup>5</sup> is not justified in comparing results expressed as lbs. per in. The results must be corrected for the difference in width. From the corrected published results and results obtained at Blackley it is clear that the angle-tear and crescent-tear specimens do not give the same result. Apart from the different stress distributions in the two samples producing different results, there is another reason for the discrepancy. The ideal tear test would measure both the force required to start a tear and the force required to make the tear grow. The present authors feel that the angle-tear test is not a replacement for the crescent test but is a useful addition. It can be used to give an indication of the force required to initiate a tear and the crescent-tear test measures the force required to continue tearing. A more detailed comparison of the two methods will be possible when the present experimental work is complete.

#### CONCLUSIONS

- (1) A new tear cutter has been designed which is capable of easy and rapid operation for routine work.
- (2) Using the new cutter accurate work is possible, and the error in tear resistance results has been reduced to the same order as that obtained with tensile strength determinations.

- (3) It is recommended that a tolerance value of  $\pm 3$  thousands inch be placed on the 0.02-inch depth of nick.
- (4) It is also recommended that six test-pieces be used, and the median of the results recorded.
- (5) The observation is made that the angle-tear test is a measure of tear initiation and can, therefore, be considered an addition to the crescent-tear test, which is a measure of tear propagation.

## REFERENCES

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- <sup>3</sup> Buist and Davies, *Trans. Inst. Rubber Ind.* **22**, 68 (1946).
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# STATISTICAL EVALUATION OF VARIATIONS IN RUBBER PROCESSES AND CORRELATION IN PHYSICAL PROPERTIES\*

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*Introduction.*—The scope for the application of statistics to the field of rubberlike materials is extensive, and various authors<sup>1</sup> have already used statistical methods. Statistical methods derive the maximum amount of information from the results of an investigation, and at the same time supply a means of assessing the reliability and value of the information extracted. The effect of a variety of different blacks at various volume loadings on the properties of natural rubber and Neoprene-GN have been described<sup>2</sup>. In the present paper the data are examined from other points of view, *viz.*, the reproducibility of the results and the relations between the various properties. The main purpose of these investigations was to obtain the technological information already reported<sup>2</sup>. At the same time, however, the program was designed as far as practicable to give information on the testing errors. Further useful information on the relation between the properties could be obtained by the application of the methods of statistical analysis.

The program of experimental work with natural rubber covered a period of three months (November 1940–February 1941) and, to obviate as far as possible variations in the raw material, a quantity sufficient for the whole program was master-batched at the outset. The carbon blacks used were from normal supply, but special quantities were kept for this program. In 1942 a similar program was carried out with Neoprene-GN. The details of the mixes used, mixing procedure, and conditions of curing, have been given previously<sup>2</sup>. Each mix was repeated three times on different days, and repeat determinations on the physical properties were carried out.

*Statistical analysis.*—Most laboratories appreciate that it is necessary to evaluate accurately the experimental errors inherent in testing methods. With rubberlike materials, however, the analysis must be carried further, and the errors or variations involved in each process must be evaluated. The main sources of errors in the laboratory or factory are (1) variations in raw materials; (2) variations in mixing (including variations in milling and mixing, preparation of the samples for cure, filling the mould, etc.); (3) variations in curing, and (4) errors due to final testing (including variations in the preparation of samples for the final test).

Variations in raw materials have not been evaluated, but precautions were taken to reduce their importance as much as possible by master batching. The other errors have been evaluated in full.

The statistical terms used in this report have been fully defined, and the statistical methods have also been described<sup>3</sup>.

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In this work  $\pm 2\sigma$  has been taken as the practical limits of error, since 95 per cent of the tests carried out fall within this range<sup>3</sup>; in other words, errors greater than  $\pm 2\sigma$  occur in the long run with a frequency of 1 in 20. When there are  $n$  results the corresponding limits of error in the mean are reduced to  $\pm 2\sigma/\sqrt{n}$ .

**Testing error.**—The physical testing of the finished samples of natural rubber was carried out in replicate and the individual repeat figures were used to calculate the testing error, *i.e.*, the error at the final stage. For example, six rings cut from the same test sheet were tested for tensile strength, and in each case these six results were used to calculate the error of test associated with tensile strength determinations. Similar methods were used with each of the properties listed in Table 1. The relevant details of the methods used to measure these properties are described in the previous paper<sup>2</sup>.

TABLE 1  
TESTING ERROR AT FINAL STAGE

Physical property	Degrees of freedom	Variance V	Standard error $\sigma = \sqrt{V}$	Mean value of test result	$\pm 2\sigma\%$	No. of repeat tests per sample	$\pm 2\sigma\%$
Tensile strength	301	48.0	6.92	190	$\pm 7.2\%$	6	$\pm 2.94\%$
Elongation at break	301	168.3	12.97	550	$\pm 4.7\%$	6	$\pm 1.92\%$
Resilience (Tripsometer)	266	0.79	0.89	80	$\pm 2.2\%$	3	$\pm 1.27\%$
Indentation (Tripsometer)	272	0.12	0.35	12.0	$\pm 5.8\%$	3	$\pm 3.35\%$
Plasticity compression	150	11.61	3.41	300	$\pm 2.2\%$	3	$\pm 1.27\%$
Plasticity recovery	123	13.98	3.74	300	$\pm 2.5\%$	3	$\pm 1.44\%$
Detrition °C 25 kg.	93	2.88	1.7	120	$\pm 3.0\%$	3	$\pm 1.73\%$
Detrition °C 50 kg.	78	3.15	1.77	150	$\pm 2.4\%$	3	$\pm 1.39\%$
Resilience (pendulum)	100	0.28	0.53	70	$\pm 1.5\%$	2	$\pm 1.06\%$
Modulus (pendulum)	94	3.09	1.76	120	$\pm 2.0\%$	2	$\pm 2.12\%$
du Pont abrasion	88	14.15	3.77	250	$\pm 3.0\%$	6	$\pm 1.23\%$

The error of test on the torsion apparatus was worked out according to the mean range method<sup>4</sup>.

The results obtained were:

Standard error of test  $\pm 2$  per cent over range 80–100 per cent resilience  
 $\pm 3$  per cent over range 60–80 per cent resilience

The error of test is given in this form as it was found that this test gave more variable results with stiffer samples, *i.e.*, at lower values of resilience and it would not therefore be strictly accurate to express the error simply as a percentage without giving the range to which that percentage error applied. A constant coefficient of variation is obtained however, if expressed as per cent of  $(100 - R)$ .

With the properties given in Table 2, the standard errors include the day-to-day variation and any variation introduced in the curing operation in addition to those in the final testing.

From the errors of test given in Tables 1 and 2 the following points are worthy of note. The measurement of elongation is not so liable to error as the measurement of tensile strength. The reason for this can be appreciated by considering a normal stress strain curve. At the upper end of the curve the elongation is changing much less than the tensile strength and therefore an accidental break produces less error in the elongation measurement.

From Table 1 it is seen that measurements of resilience are less liable to error than measurements of modulus. The explanation is presumably that resilience is relatively insensitive to previous history, whereas modulus is very sensitive to previous history.

TABLE 2

Physical property	Degrees of freedom	Variance $V$	Standard error $\sigma = \sqrt{V}$	Mean value	$\pm 2\sigma\%$
Shore hardness	64	2.19	1.48	55	$\pm 5.4\%$
R.A.B.R.M. hardness	60	8.13	2.85	90	$\pm 6.3\%$
Swelling in benzene 1 day	52	27.81	5.27	250	$\pm 4.2\%$
2 days	52	25.28	5.03	250	$\pm 4.0\%$
Modulus high frequency:					
WT .0	48	11.43	3.38	100	$\pm 6.75\%$
WT .958	46	9.27	3.94	90	$\pm 6.8\%$

With the du Pont abrasion test the coefficient of variation of 3 per cent is small. This shows that it is not inaccuracies in the machine which are responsible for the lack of correlation with service but that there is some factor in abrasion which is either missing entirely, *e.g.*, time of recovery, or some factor which is over or under emphasized.

**Total laboratory error.**—Three repeat test samples, including three separate mixings and cures, were prepared for each volume loading of all the grades of carbon blacks. The variation in the results of the three replicates enables an estimate to be made of the total laboratory error<sup>5</sup>. The detailed results have been reported separately<sup>2</sup>.

That part of the total laboratory error which is due to processing can be readily separated, as the error has already been determined at the final testing stage, *e.g.*, if  $V_T$  = variance of test,  $V_p$  = variance of processing and  $V$  = total variance,  $V = V_T/n + V_p$  where  $n$  = number of repeat tests at the final stage. It is also possible to determine that part of the processing error which is due to cure. The method is as follows.

With each volume loading the series of blacks were cured together in the autoclave, as was also the case with the repeat mixes. It is, therefore, possible to arrange the results in a series of tables as follows:

	Cure 1	Cure 2	Cure 3
Black 1	$a_1$	$a_2$	$a_3$
Black 2	$b_1$	$b_2$	$b_3$
Black 3	$c_1$	$c_2$	$c_3$
Black 4	$d_1$	$d_2$	$d_3$

Where  $a$ ,  $b$ ,  $c$  and  $d$  are the actual results obtained for the property under consideration.

This form of table lends itself to the analysis of variance<sup>6</sup>.

The variance due to cure, variance due to the blacks, and the remainder variance can be separated and assessed. The remainder variance is largely composed of the mixing variance, but it includes the testing variance, *i.e.*,

includes all the variance apart from that introduced at the curing stage, except for variability inside the autoclave. The latter is considered to be small.

By separating out the variances as illustrated above it is possible to find the variance due to cure and the variance due to mixing, i.e.:

$$V_M = V_P - V_C$$

and

$$V_M = V_R - V_T$$

The results obtained by the preceding three methods are grouped together and included in Table 3.

TABLE 3

Test	$\pm 2\sigma\%$ Testing mean	$\pm 2\sigma\%$ curing	$\pm 2\sigma\%$ mixing	$\pm 2\sigma\%$ Processing	$\pm 2\sigma\%$ Total lab. error
Tensile strength	$\pm 2.9\%$ (6)	$\pm 3.5\%$	$\pm 6.6\%$	$\pm 7.6\%$	$\pm 8.1\%$
Elongation	$\pm 1.9\%$ (6)	$\pm 6.6\%$	$\pm 3.74\%$	$\pm 7.6\%$	$\pm 8\%$
Tripsometer resilience	$\pm 1.1\%$ (4)	not signif.	$\pm 2.24\%$	$\pm 2.6\%$	$\pm 2.81\%$
Indentation	$\pm 2.9\%$ (4)	$\pm 3.88\%$	$\pm 2.06\%$	$\pm 4.4\%$	$\pm 5.2\%$
Detrition ° C	$\pm 2.1\%$ (2)	not signif.	$\pm 3.5\%$	$\pm 3.8\%$	$\pm 4.3\%$
25 kg.					
50 kg.	$\pm 1.7\%$ (2)	$\pm 1.82\%$	$\pm 3.78\%$	$\pm 4.2\%$	$\pm 4.5\%$
Dyn. resilience	$\pm 1.5\%$ (1)	$\pm 2.08\%$	$\pm 1.35\%$	$\pm 2.5\%$	$\pm 2.7\%$
Dyn. modulus	$\pm 3\%$ (1)	$\pm 1.11\%$	$\pm 5.84\%$	$\pm 6\%$	$\pm 6.25\%$
Torsional resilience	$\pm 1.5\%$ (4)	$\pm 0.22\%$	$\pm 2.58\%$	$\pm 2.6\%$	$\pm 2.96\%$
du Pont abrasion	$\pm 2.1\%$	$\pm 8.6\%$	$\pm 12.04\%$	$\pm 13.2\%$	$\pm 13.4\%$
Plasticity:					
Comp.	$\pm 1.3\%$ (3)	not signif.	$\pm 10\%$	$\pm 10\%$	$\pm 10.3\%$
Recovery	$\pm 1.44\%$ (4)	not signif.	$\pm 14\%$	$\pm 14\%$	$\pm 14.2\%$
Shore hardness	$\pm 2.2\%$ (4)	$\pm 3.1\%$	$\pm 4.1\%$	$\pm 5.48\%$	$\pm 6.1\%$
R.A.B.R.M. hardness	$\pm 3.1\%$ (3)	not signif.	$\pm 6.9\%$	$\pm 7.0\%$	$\pm 7.75\%$
H. F. modulus:					
WT .0	$\pm 6.7\%$ (1)	$\pm 8.7\%$	$\pm 16.2\%$	$\pm 17.3\%$	$\pm 17.8\%$
WT .958	$\pm 6.8\%$ (1)	$\pm 6.9\%$	$\pm 10.4\%$	$\pm 11.5\%$	$\pm 12.0\%$
Swelling:					
1 day	$\pm 4.2\%$ (1)	not signif.	$\pm 2.84\%$	$\pm 3\%$	$\pm 5.1\%$
2 days	$\pm 4.0\%$ (1)	not signif.	$\pm 6\%$	$\pm 6.3\%$	$\pm 7.1\%$

The figures in brackets in column (1) indicate the number of repeat tests that were done on each sample.

From Table 4 it is seen that:

- (1) In practically every case the estimated error due to mixing is larger than the error due to curing. There are three exceptions to the above and these are (1) elongation, (2) indentation and (3) dynamic resilience.
- (2) As a general rule hardness or modulus tests are more sensitive to processing variations than are tests measuring resilience.

**Discriminating Power.**—The various tests discriminate between the grades of carbon blacks to varying extents<sup>7</sup>. The discriminating power may be defined as the ratio of the variance between the blacks to the total error variance. The 10-volume loading was used for all the blacks and is, therefore, convenient for the determination of the discriminating power (*D*). To calculate this for



TABLE 4

Test	Error variance $E$	Variance between carbon blacks $V$	$D = 3V/E$
Tensile strength	93	185	6.0
Elongation	707	1779	7.6
S. hardness	1.14	14	36.8
R.A.B.R.M.	18.43	107	17.5
Elasticity (Shore)	1.57	.17	0.4*
Permanent set	4.79	2.29	1.4*
Resilience trips	1.01	12.0	36
Indentation	.135	.32	7.1
du Pont abrasion	910	6005	19.8
Stress strain: 100%	11	3.8	1.0*
200%	16.4	32.5	5.9
300%	26.4	147	16.7
400%	56	443	23.7
500%	152	1018	20.1
600%	1359	1579	3.5
Detrition ° C: 25 kg.	16	97	18.2
50 kg	11.36	346	91
Swelling: 1 day	950	433	1.4*
2 days	1005	488	1.5*
Dynamic resilience	1.00	7.5	23
modulus	2.14	33.0	46
H. F. modulus: WT .0	1.79	81.4	136
WT .958	4.14	88.5	64

\* The discriminating power in these cases is not significant.

each test the following will be required: (1) the variance  $V$ , of the mean test for the given volume loading between the various carbon blacks; and (2) the error variance of each mean. If  $E$  is the total laboratory variance for each sample, then the variance of the mean of the three samples is  $E/3$ .

Hence  $D = 3V/E$ .

To be considered significant at the 5 per cent level,  $D$  should have a value greater than 2.96, and for 1 per cent level  $D$  should have a value greater than 4.69.

From Table 4 it is seen that the Shore elastometer has no discriminating power. With stress-strain results it is interesting to note that the discriminating power passes through a maximum at 400 per cent. This endorses the practice of measuring modulus at elongations of 300 per cent and 500 per cent. The fact that the swelling test has no significant discriminating power at this small loading of black is self-explanatory, as it is the rubber structure that is being swollen.

Table 5 gives a comparison of the total laboratory error and the discriminating power for a few of the tests.

TABLE 5

Test	Total laboratory error	Total laboratory error ( $\pm 2\sigma$ %)
H. F. modulus: WT .0	$\pm 17.8\%$	136
WT .958	$\pm 12.0\%$	64
Detrition ° C: 25 kg.	$\pm 4.3\%$	18.2
40 kg.	$\pm 4.5\%$	91
Tripsometer resilience	$\pm 2.81\%$	36
Dynamic resilience	$\pm 2.7\%$	23
Dynamic modulus	$\pm 6.25\%$	46
Shore hardness	$\pm 6.1\%$	36.8
R.A.B.R.M. hardness	$\pm 7.75\%$	17.5
Indentation	$\pm 5.2\%$	7.1

Both hardness methods, *e.g.*, Shore and R.A.B.R.M., have higher discriminating powers than indentation measurements on the tripsometer. In the detrition test the higher load of 50 kilograms has a much higher discriminating power than the 25-kg. load, both conditions of test having approximately the same per cent total laboratory error.

**Correlation Coefficients.**—A correlation coefficient is an overall measure of the extent of linear relationship between two tests, *i.e.*, the extent to which the two tests measure the same property if the relationship is linear. This statistic is usually denoted by  $r$  and may have a value between  $-1$  and  $+1$ . A positive correlation indicates that an increase in the value of one test is accompanied by an increase in the value of the other test. A negative correlation, on the other hand, indicates that the two tests vary in opposite directions. The larger the value of  $r$ , irrespective of sign, the closer the relationship between the tests;  $0$  indicates zero relationship while  $\pm 1$  indicates perfect relationship<sup>5</sup>.

If  $r$  is the correlation between properties  $x$  and  $y$ , then the relationship between  $x$  and  $y$  is expressed by:

$$\frac{(y - \bar{y})}{\sigma_y} = \frac{r(x - \bar{x})}{\sigma_x}$$

$$i.e., \quad y = r \frac{\sigma_y}{\sigma_x} (x - \bar{x}) + \bar{y}$$

where  $\bar{y}$  and  $\bar{x}$  are the average values of these properties and  $\sigma_y$  and  $\sigma_x$  their standard deviations over the range examined.

$$i.e., \quad \begin{array}{l} \text{range of values of } y \text{ is approx. } \bar{y} \pm 2.58 \sigma_y \\ \text{and that of } x \text{ is approx. } \bar{x} \pm 2.58 \sigma_x \end{array}$$

(mean  $\pm 2.58\sigma$  represents 99 per cent of the range of variation, as deviations greater than  $\pm 2.58\sigma$  occur with a frequency of 1 in 100).

It is usually desirable to quote the range of values of the test whenever a correlation coefficient is being considered.

Another method of interpreting a correlation coefficient  $r$  between the variates  $x$  and  $y$  is that a proportion  $r^2$  of the variation in the property  $y$  can be accounted for by variations in  $x$ . In other words, of the total variance  $V_y$  of  $y$  an amount  $r^2 V_y$  is due to the variate  $x$ . To take an actual example the correlation between Shore hardness and du Pont abrasion was found to be  $-0.729$ .

$$\begin{array}{ll} \sigma_{abr.} = 68.9 & V_{abr.} = 4743.4 \\ \sigma_{S.H.} = 11.1 & V_{S.H.} = 122.7 \\ r^2 = (-0.729)^2 = 0.531 \end{array}$$

Accordingly, 53.1 per cent of the variation, *i.e.*, variance, of 4743.4 observed for abrasion is due to variations in the Shore hardness.

The correlation coefficients between all properties taken in pairs are given in Table 6. In all cases where the variables were related, the relationship is substantially linear, therefore, the correlation coefficients are satisfactory measures of the extent of the relationships.

The following points arising out of Table 6 are worthy of note.

(1) Shore hardness gives the highest direct correlation with abrasion resistance as measured on the du Pont machine.

(2) Tensile strength is not highly correlated with any other property; the highest correlation being  $+0.534$  with torsional resilience.

TABLE 6

	Abrasion	Tensile strength	Elongation	Shore hardness	R.A.B.R.M.	Resilience 50° C	Indentation	Stress strain 300%	Benzene swelling	Detrition ° C 1000 revs.	Dynamic resilience	Dynamic modulus	High frequency modulus	Plasticity	Torsional resilience
Abrasion	1	.291	.498	.729	.711	.417	.701	.625	.560	.061	.462	.584	.576	.453	.491
Tensile	.291	1	.316	.258	.298	.462	.252	.114	.095	.390	.399	.424	.361	.290	.534
Elongation	.498	.316	1	.847	.759	.355	.818	.965	.857	.125	.351	.631	.501	.309	.538
S. Hardness	.729	.238	.847	1	.971	.716	.977	.800	.694	.255	.729	.877	.835	.673	.817
R.A.B.R.M.	.711	.298	.759	.971	1	.774	.944	.759	.606	.361	.799	.912	.870	.699	.855
Resilience 50° C	.417	.462	.355	.716	.774	1	.746	.330	.019	.832	.963	.848	.942	.922	.948
Indentation	.701	.252	.818	.977	.944	.746	1	.835	.650	.295	.726	.849	.800	.746	.819
Stress strain 300%	.625	.114	.965	.800	.759	.330	.835	1	.901	.167	.333	.612	.503	.323	.499
Benzene swelling	.560	.095	.857	.694	.606	.019	.650	.901	1	.469	.063	.380	.244	.424	.192
Detrition ° C 1000 revs.	.061	.390	.125	.255	.361	.832	.295	.167	.469	1	.821	.543	.647	.720	.690
Dynamic resilience	.462	.399	.351	.720	.799	.963	.726	.333	.063	.821	1	.922	.922	.818	.936
Dynamic modulus	.584	.424	.631	.877	.912	.848	.849	.612	.380	.543	.908	1	.905	.689	.936
High-frequency modulus	.576	.361	.501	.835	.870	.942	.860	.503	.244	.647	.922	.905	1	.901	.954
Plasticity	.453	.290	.309	.673	.699	.922	.746	.323	.424	.720	.818	.689	.901	1	.834
Torsional resilience	.491	.534	.538	.817	.855	.948	.819	.499	.192	.690	.936	.936	.954	.834	1

(3) Elongation has a high correlation with modulus at 300 per cent, which can be interpreted as follows: the higher the modulus of the stock, the lower the elongation at break.

(4) Both elongation and modulus at 300 per cent have a high correlation with swelling in benzene.

(5) All tests measuring hardness are highly correlated, and over this range of compounding in natural rubber no appreciable extra information is obtained by R.A.B.R.M. hardness or indentation results over the results obtained on the Shore durometer, or *vice versa*.

(6) It is interesting to note that plasticity compression measurements have a high correlation with all measurements of resilience and also with high-frequency modulus.

(7) It can be noted that hardness (measured on Shore durometer) is fairly highly correlated with all tests except tensile strength and detrition. It follows, therefore, that, apart from these two properties, the tests made on rubber are largely hardness tests, *e.g.*, indentation and R.A.B.R.M. Hardness are almost entirely hardness, elongation, stress-strain 300 per cent, and the other two modulus tests, dynamic modulus and high-frequency modulus, are more than 70 per cent hardness; all resilience measurements and abrasion resistance (du Pont machine) are 50 per cent or more due to hardness.

In the preceding paragraph the term, hardness, refers to the property as measured on the Shore durometer.

*Neoprene-GN*.—The degree of correlation between each property would not be expected to be the same for all rubbers and, although the variations may in general be slight, they are nevertheless important. A program<sup>2</sup> of work similar to the natural rubber program was carried out with Neoprene-GN. The correlation coefficients between some physical properties taken in pairs are given in Table 7.

TABLE 7

	Tensile strength	B.S.I. hardness	Shore hardness	Resilience	Tear resistance	du Pont abrasion	Dunlop abrasion	Detrition
Tensile strength	1	0.25	-0.30	0.23	0.67	-0.30	-0.73	0.37
B.S.I. hardness	0.25	1	-0.98	0.92	0.15	0.71	0.14	0.94
Shore hardness	-0.30	-0.98	1	-0.94	-0.25	-0.74	-0.13	-0.95
Resilience	0.23	0.92	-0.94	1	0.25	0.73	0.15	0.96
Tear resistance	0.67	0.15	-0.25	0.25	1	-0.07	-0.49	0.04
du Pont abrasion	-0.30	0.71	-0.74	0.73	-0.07	1	0.64	0.74
Dunlop abrasion	-0.73	0.14	-0.13	0.15	-0.49	0.64	1	0.37
Detrition	0.37	0.94	-0.95	0.96	0.04	0.74	0.37	1

The Thermax results were not included in the calculations.

From Table 7 the following points should be noted:

- (1) All tests measuring hardness are highly correlated.
- (2) B.S. hardness, Shore hardness, resilience, and detrition are all highly correlated with one another.
- (3) The correlation of tensile strength with other physical properties is poor except with tear resistance<sup>3</sup> and Dunlop abrasion resistance.
- (4) The correlation between resilience and Dunlop abrasion resistance is small.
- (5) The correlation of detrition with other physical properties is positive in the case of Neoprene-GN but is negative for the same properties with natural

rubber. At present no completely satisfactory explanation of this can be given.

(6) The correlation of resilience with other physical properties, except tensile strength, is much higher in the case of Neoprene-GN than with natural rubber.

This can be seen easily from Table 8, where the correlations between resilience and other physical properties are given for both rubbers.

TABLE 8  
CORRELATION OF RESILIENCE AND OTHER PHYSICAL PROPERTIES

	Tensile strength	R.A.B.R.M. hardness	B.S.I. hardness	Shore hardness	du Pont abrasion	Detrition
Natural rubber	0.462	0.774	—	-0.716	0.417	-0.832
Neoprene-GN	0.23	—	0.92	-0.94	0.73	0.96

Unfortunately, resilience was measured under only one set of conditions with Neoprene-GN and the extent of the effect of testing conditions (temperature, speed, etc.) is not known, although it is undoubtedly important.

All the properties, except resilience, show good agreement between the values obtained for natural rubber and Neoprene-GN. Since 1941, the B.S. hardness instrument has replaced the R.A.B.R.M. instrument. The correlation coefficients between these properties measured on these instruments and the other physical properties are of the same order for both rubbers, and this can be taken to indicate that the same basic property is being measured by both the B.S. and R.A.B.R.M. methods.

*Multiple correlations for natural rubber.*—Taken separately, Shore hardness and tensile strength are not highly correlated with abrasion, abrasion and tensile strength being  $-0.291$  and abrasion and Shore hardness being  $-0.729$ . However, taking both hardness and tensile strength together it is found that the correlation is  $0.882$ . In other words, hardness and tensile strength together account for  $(0.882)^2 = 78$  per cent of abrasion variations. It can, therefore, be stated that the mechanism of abrasion resistance as measured on the du Pont machine can be explained to the extent of nearly 80 per cent by hardness and tensile strength alone.

If elongation is also included the correlation is improved very slightly to  $0.892$ , and including all other tests the correlation is increased only to  $0.895$ .

Thus it is evident that it is impossible to account for the greater part of the 20 per cent of abrasion variations with the present tests. Some are, of course, due to testing errors. Apart from this missing factor of 20 per cent, it is clear that all tests other than Shore hardness and tensile strength are superfluous for the explanation of abrasion resistance as measured on the du Pont machine.

The multiple regression equation connecting du Pont abrasion with Shore hardness and tensile strength is:

$$\text{du Pont abrasion} = -5.347 \times \text{Shore hardness} - 1.039 \times \text{tensile strength} + 766.0$$

With the above equation it is, therefore, possible to estimate the abrasion loss on the du Pont machine from a known Shore hardness and a known tensile strength. The order of accuracy in the predictions may be indicated by Table 9, where the formula has been used for Kosmos-T and Shawinigan blacks.

There is good agreement between the actual and calculated results.

The equation cannot, of course, be expected to hold for any point appreciably outside the ranges of hardness and tensile strength actually encountered in this investigation. The fact that a wide divergence is obtained with the 50-vol. loading of Kosmos-T is due to the fact that it is past the optimum loading of the black (optimum for abrasion resistance is 30 volumes), and much of the the black present is doing no useful work from an abrasion resistance point of view. The figure 59 represents the abrasion loss which would be obtained if all the black were reinforcing the rubber.

It is possible to obtain an estimate of the error in the above forecast of the abrasion loss when the tensile strength and hardness are known. The variance of the estimate is:  $V_{abr.} \times (1 - R^2)$  where  $V_{abr.}$  is the variance of the abrasion results and  $R$  the multiple correlation. This gives  $4744 (1 - (0.882)^2) = 1053$ , which corresponds to a standard error of 32 for the estimate of abrasion.

TABLE 9

Black	Tensile strength	Shore hardness	Actual abrasion loss	Calculated abrasion loss
Kosmos-T 10 vols.	210	49	320	286
15 vols.	254	56	235	203
20 vols.	255	60	190	180
25 vols.	254	65	167	154
30 vols.	249	70	152	133
50 vols.	192	85	141	759
Shawinigan 10 vols.	233	48	242	267
15 vols.	237	57	206	215
20 vols.	217	63	167	197
25 vols.	211	68	155	183

The estimate of the abrasion may, therefore, be in error by  $\pm 2\sigma = \pm 64 = \pm 26$  per cent on an average figure of 250. Errors greater than  $\pm 2\sigma$  occur with a frequency of 1 in 20. It is noted that the error in this estimate, i.e.,  $\pm 2\sigma$  per cent, contains the total laboratory error of  $\pm 13.4$  per cent, and therefore this form of prediction is a useful guide as to what can be expected from certain known values of tensile strength and Shore hardness.

*Heat build-up.*—With the same technique the following equation is constructed for heat build-up as measured on the Schopper-Martens test under a load of 25 kilograms.

Detrition (heat build-up) =  $480.2 - 2.374$  shore hardness  $- 3.668$  resilience.

In this case hardness and resilience account for 93 per cent of heat build-up variations. Elsewhere<sup>9</sup> it has been stated that in a given type of service, the heat developed ( $H$ ) is governed by the formula:

$$H = (100 - r)E/100$$

where

$E$  = energy input, and  $r$  = resilience per cent.

Under conditions of constant load this equation becomes:

$$H = (100 - r) \frac{F^2/100}{2S}, \text{ where } F = \text{force and } S = \text{stiffness,}$$

and again it is possible to calculate the relative heat developed per cycle from a knowledge of resilience and stiffness alone.



From the detrition equation, it is possible to calculate the heat build-up, and Table 10 shows a comparison of the calculated and observed values for samples selected at random.

Within the limits of this investigation, it will be seen that if hardness is maintained constant and resilience improved, the heat build-up decreases. Similarly if resilience is maintained constant and hardness increased, the heat build-up decreases.

TABLE 10

Black	Hardness (Shore)	Resilience at 50° C (%)	Heat build-up observed	Heat build-up calculated
30 vols. Thermax	48	80.9	65° C	69.5° C
30 vols. P-33	52	75.9	72° C	78.4° C
30 vols. SBI	59	75.7	68° C	62.5° C
25 vols. Magecol	60	70.0	77° C	81° C
20 vols. Kosmos-T	60	63.8	116° C	104° C
20 vols. Kosmos F .4	60	40.8	192° C	188° C
20 vols. Shawinigan	63	69.7	81° C	75° C
50 vols. P-33	64	67.3	78° C	81° C
25 vols. Kosmos-T	65	59.4	119° C	108° C
25 vols. Shawinigan	68	63.6	84° C	85° C
50 vols. SBI	74	66.1	69° C	62° C

*Use of statistical equations.*—Since 1941 the shortage of natural rubber has necessarily restricted the use of these equations. Even so, it has been possible to test them in various problems, and as long as the properties lay within the range of values used in these calculations good correlation between calculated and observed values was obtained. Anomolous results may be obtained with fillers other than carbon blacks and also with gross under- or overcures. The same equations do not apply when the rubber phase is changed to that of a synthetic rubber. The results obtained with Neoprene-GN illustrate this point. Using the same technique as described previously, the following equations have been constructed.

#### *Neoprene-GN*

du Pont abrasion loss =  $885.2 - 6.571 \times \text{Shore hardness} - 1.374 \times \text{tensile strength}$ .

du Pont abrasion loss =  $241.39 + 2.859 \times \text{B.S. hardness} - 1.222 \times \text{tensile strength}$ .

Heat build-up =  $5.871 \times \text{resilience} - 299.1$

Abrasion loss on Dunlop machine =  $0.684 - 0.00312 \times \text{Shore hardness} - 0.00186 \times \text{tensile strength}$ .

*Abrasion loss.*—When the natural-rubber equation for du Pont abrasion loss was constructed, it was thought that the inclusion of a tear test might account for at least part of the unaccounted 20 per cent. However, a tear test<sup>9</sup> was included in the Neoprene-GN work, and it was shown that there was no improvement in the correlation. In this case 85 per cent of the abrasion loss could be accounted for by hardness and tensile strength alone. The position with the Dunlop machine is worse for in this case only 67 per cent of the abrasion loss is accounted for by variations in hardness and tensile strength, and the remaining 33 per cent cannot be represented by any other single property. Properties such as cut propagation and cut growth must be important in abrasion resistance and if in a test the conditions are imitated under which they occur in laboratory abrasion machines, it may still be possible to account

for the missing factors. The main difference between the du Pont and Dunlop machines is that in the Dunlop machine the rubber is allowed to relax between successive impacts; in the du Pont apparatus the rubber is held continuously against the abrasive. One might presume that resilience would, therefore, be an important factor in the Dunlop apparatus, but the results do not confirm this and there is still 33 per cent which remains to be accounted for when resilience measurements are included. This may be due to the fact that the range of resilience values obtained with different carbon blacks in Neoprene-GN is small, and the point is being checked by further work.

The correlation between the two abrasion tests is not of a high order, the value being only 0.64. Although both abrasion tests are mainly functions of hardness and tensile strength, the proportions of these properties which make up the two abrasion tests are quite different. This can be seen by taking the ratio of the coefficients of Shore hardness to tensile strength which is 4.8 for the du Pont test and 1.7 for the Dunlop machine.

The standard error of the predictions for du Pont abrasion is 34, *i.e.*, 19 per cent, whereas for the Dunlop abrasion it is much larger, 0.045, *i.e.*, 39 per cent.

*Heat build-up.*—With Neoprene-GN, B.S. hardness, Shore hardness, resilience and detrition (excluding the single results for Thermax) are all very highly correlated with one another. The correlation of heat build-up with resilience is as high as 0.97, which only leaves 6 per cent of the variations in heat build-up to be accounted for, and this can readily be due to testing errors. It has been noted previously that the correlation of heat build-up with other physical properties is positive in the case of Neoprene-GN, but is negative with natural rubber.

When the single result on Thermax is included, the correlation between detrition and resilience drops to 0.84. The correlation with detrition is not improved by including hardness; there is no point, therefore, in constructing a multiple regression equation for detrition in terms of resilience and hardness.

*Conclusions.*—The total laboratory error has been obtained for most of the physical properties of rubberlike materials. The variations introduced at the processing stage have been separated from the variations introduced by testing. The processing variations have been divided into mixing and curing variations and, in general, the errors due to mixing are larger than the errors due to curing.

A method of estimating the discriminating power of a particular test is shown. The measurement of elongation is not so liable to error as the measurement of tensile strength.

The correlation coefficients between different physical properties have been evaluated. Tensile strength is not highly correlated with any other single property. Elongation has a very high correlation with modulus at 300 per cent, and both these properties have a high correlation with swelling in benzene. All tests measuring hardness are very highly correlated. Shore hardness gives the highest direct correlation with abrasion resistance as measured on the du Pont machine. The degree of correlation between each property is not the same for all rubbers, and the correlations for the physical properties of Neoprene-GN are given. The correlation of resilience with other physical properties is, in general, much higher in the case of Neoprene-GN than with natural rubber.

With multiple correlations it is possible to construct equations for du Pont abrasion resistance and heat build-up with natural rubber. Abrasion resistance

as measured on the du Pont machine can be explained to the extent of nearly 80 per cent by hardness and tensile strength alone. There is good agreement between the actual and calculated results. Similar equations are given for Neoprene-GN. In addition, an equation is given for abrasion resistance as measured on a Dunlop type of machine. In this case only 67 per cent of the abrasion loss is accounted for, and it is clear that the mechanism of abrasion loss as measured on the two types of laboratory abrasion machines differs fundamentally. Although both abrasion tests are mainly functions of hardness and tensile strength, the proportions of these properties which make up the two tests are appreciably different.

The above equations are obtained from results of carbon-black loaded stocks of natural rubber and Neoprene-GN. Sufficient work has not yet been done to establish the exact limits of their application. Meanwhile if they are applied to results outside the scope of the above program the results should be interpreted with caution.

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# VULCANIZATION TESTING OF RECLAIM. RELATION BETWEEN RESULTS OBTAINED IN RECLAIM-SULFUR AND TIRE-TREAD MIXES \*

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## INTRODUCTION

It is generally agreed that the best way of assessing the value of a reclaim is by a vulcanization test. Practice varies, however, in regard to the type of mix used. Extensive use has been made of a simple reclaim-sulfur mix, proportions of 100:5 being generally adopted<sup>1</sup>, often with a fixed vulcanizing period. As long ago as 1926, however, it was shown<sup>2</sup> that the tensile properties of reclaim-sulfur vulcanizates bear no obvious relationship to those of mixes containing also a substantial proportion of new rubber (rubber/reclaim ratio, 58:24) plus an accelerator; moreover, reclaims that varied widely in the reclaim-sulfur mix (tensile strength 200 to 1,390 lbs. per sq. in.) gave much the same results in the accelerated rubber mix (2,600 to 3,050 lbs. per sq. in.).

Subsequently other data have been published which confirm the absence of a close relationship between reclaim-sulfur mixes and those where the reclaim is used to replace part of the new rubber<sup>3</sup>. Even when the proportion of reclaim equals or exceeds that of new rubber, moderate differences between reclaims as shown by the reclaim-sulfur mix, may practically disappear, although when the proportion of reclaim is very high, the differences may persist in a reduced degree<sup>4</sup>. The unreliability of the reclaim-sulfur mix is referred to by many other writers<sup>5</sup>; in particular it is stated that the higher the rubber hydrocarbon content of a reclaim the poorer are the tensile figures for the all-reclaim mix, apparently due to the lack of reinforcing fillers<sup>6</sup>, and that tensile test results on such a mix are unusually variable and susceptible to changes in test-room temperature<sup>7</sup>. Stafford<sup>8</sup>, however, considers that a low tensile strength indicates a "coarser" product liable to give inferior results in commercial mixes.

Evidence regarding the advantages of an accelerated reclaim-sulfur test mix is conflicting. Winkelmann<sup>2</sup> found that the addition of an organic accelerated reclaim-sulfur test mix is conflicting. Winkelmann<sup>2</sup> found that the addition of an organic accelerator, without zinc oxide, to reclaim-sulfur mixes did not markedly alter the tensile strength or reduce the variation between reclaims, but Hurleston<sup>9</sup> found that accelerator plus zinc oxide greatly reduced, though it did not eliminate, the differences; he accordingly recommended using "a fixed amount of a standard accelerator". (The choice of accelerator is discussed by Palmer and Crossley<sup>10</sup>). On the other hand, Wallace<sup>6</sup> and Yosida<sup>11</sup> consider even the reclaim-sulfur-accelerator-zinc oxide type of mix unreliable because differences are still exaggerated and unrelated to those found in commercial mixes containing the reclaims.

Addition of quite a moderate proportion of new rubber, e.g., 20 parts per 100 parts of reclaim, may greatly reduce the differences between reclaims as

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judged by the tensile properties of the vulcanizates, and accordingly has been recommended in the testing of reclaims. A new-rubber/reclaim ratio of 10:100, plus an accelerator, showed big differences between various types of reclaim, these differences being generally produced in a smaller degree in commercial mixes containing much larger proportions of new rubber<sup>12</sup>.

The reclaim-sulfur mix, however, in spite of its limitations, still seems to be quite often used, and indeed appears in comparatively recent papers<sup>13</sup>. Tests on a large number of reclaims have been carried out on behalf of the Ministry of Supply, and the data are used in this report with the permission of the Ministry.

The reclaims were tested in a reclaim-sulfur mix and a degraded tire-tread mix; the tensile properties and hardness of the former are compared with the corresponding properties, and also the abrasion and flex-cracking resistance, of the latter. Observations are recorded also on (1) the relation between abrasion and flex-cracking and the tensile properties of the tread mix, (2) accelerated aging of the reclaim-sulfur vulcanizates.

### EXPERIMENTAL METHODS

Full particulars of the reclaims used were not always available, but they were mostly made from whole-tire scrap, and comprised alkali, neutral, and thermal types, as well as samples made by special processes.

The mixes used were:

	Reclaim-sulfur	Tire tread
Smoked sheet	—	80
Reclaim	95	40
Sulfur	5	3
Channel black*	—	40
Zinc oxide	—	4
Stearic acid	—	2.5
Mercaptobenzothiazole	—	0.8

\* Normal "dustless" type.

Each mix was vulcanized for various periods at 141° C (reclaim-sulfur) or 148° C (tire tread) so that the optimum vulcanizing period could be determined. Tensile and hardness tests were made according to B.S. 903-1940, and permanent set measured by stretching to 200 per cent elongation for 15 minutes and allowing to recover or 60 minutes. Abrasion-resistance was measured on the Akron machine and flex-cracking resistance on the De Mattia machine, in both cases using the standard technique<sup>14</sup>.

### RESULTS

Test data for optimum-vulcanized samples are given in Tables 1 and 2, under the following abbreviations:

Vulc. = optimum vulcanizing period (min.)

TS = tensile strength of dumb-bell specimens (lbs. per sq. in.)

EB = elongation at break (percentage)

M100, M300 = moduli (lbs. per sq. in. at 100 and 300 per cent elongation)

H = British Standard hardness number on rubber specimens (5 mm. thick)

PS = permanent set (percentage)

AA = Akron abrasion loss cc. per 1,000 revolutions

Flex = flex-cracking resistance (number of kilocycles to reach standard degree of cracking)

TSA, EBA = TS and EB after 10 days, Geer oven aging at 70° C, expressed as percentage of unaged values.

TABLE 1  
TIRE TREAD MIXES

Reclaim		Vulc.	TS	EB	M100	M300	H	PS	AA	Flex
No.	Type									
1	WT/A	15	3960	520	320	1700	63	—	0.315	66
2	WT/A	15	3580	515	260	1660	53	7.0	0.245	75
3	WT/A	15	3900	580	240	1220	65	4.0	0.310	190
4	WT/A	10	3760	510	430	1860	52	8.0	0.235	64
5	WT/A	20	3580	510	410	1740	51	7.5	0.335	55
6	WT/A	17	3200	540	220	1110	69	4.3	0.295	140
7	WT/A	20	3080	460	260	1640	70	—	0.320	38
8	WT/A (a)	20	3440	430	540	2270	35	12.0	0.250	24
8A	WT/A	15	3800	550	310	1570	62	4.5	0.290	—
9	WT/N	30	3000	460	280	1590	64	—	0.300	25
10	WT/Th	20	2880	460	330	1600	65	—	0.325	59
11	WT/Th	33	2560	460	500	1470	50	—	0.445	18
12	WT/Th	30	2740	440	470	1720	52	10.0	0.295	20
13	WT/Th	30	2820	430	360	1720	53	8.5	0.210	20
14	WT/Th	25	3220	500	320	1540	56	6.5	0.230	45
15	WT/Th	25	2640	420	360	1680	58	6.5	0.290	57
16	?/Th	20	3520	490	360	1840	65	—	0.245	40
17	?/Th	25	3500	510	300	1650	54	—	0.235	28
18	?/Th	30	3140	520	320	1380	74	5.5	0.345	93
19	WT/? (b)	20	2720	445	630	1680	33	21.0	0.340	9
20	WT/? (b)	30	2300	525	280	1000	56	9.0	0.265	40
21	WT/? (c)	20	2540	410	490	1740	52	12.0	0.320	21
22	TT/? (c)	30	2780	400	460	1990	52	10.0	0.200	16
23	TT/? (c)	30	2720	420	460	1790	55	9.0	0.225	12
24	?/? (d)	25	2450	420	500	1570	55	—	0.330	17
25	?/? (d)	25	2650	425	370	1650	52	—	0.215	18
26	?/? (d)	25	2500	410	340	1580	58	7.0	0.220	15

(a) so-called tire-tread reclaim, made by adding 10 per cent of carbon black to a whole-tire reclaim during refining.

(b) Nos. 19 and 20 were made by the same process.

(c) Nos. 21-23 were made by the same process.

(d) Nos. 24-26 were made by the same process.

In the 2nd column WT denotes whole tire; TT tire tread; A alkali; N neutral; Th thermal; ? raw material or process not known.

TABLE 2  
RECLAIM-SULFUR MIXES

Reclaim no.	Vulc.	TS	EB	M100	M300	H	TSA	EBA
1	30	1450	520	95	510	—	110	75
2	33	820	345	115	550	93	175	72
3	30	1100	400	180	660	103	120	95
7	30	740	390	105	505	—	115	67
8A	35	1480	480	200	600	95	100	75
9	35	400	365	90	340	—	155	55
10	30	310	180	240	—	—	133	68
11	33	650	75	—	—	48	145	55
12	35	350	195	220	—	105	210	50
14	35	1080	320	280	1000	80	97	58
15	30	740	280	280	—	85	85	48
16	40	900	280	180	—	—	125	63
17	25	1000	370	140	700	121	140	65
18	40	560	290	280	—	104	130	52
24	40	320	250	140	—	—	210	32
25	35	350	360	70	280	—	210	72
26	37	720	280	175	—	114	80	55



## DISCUSSION

## RELATION BETWEEN CORRESPONDING PROPERTIES OF THE RECLAIM-SULFUR AND TIRE-TREAD MIXES

There is a tendency for the alkali reclaims to give quicker vulcanization than the other types in the tread mix, but this is not evident in the reclaim-sulfur mix, so the latter evidently cannot be used for predicting the effect of a reclaim on the vulcanizing rate of a commercial mix.

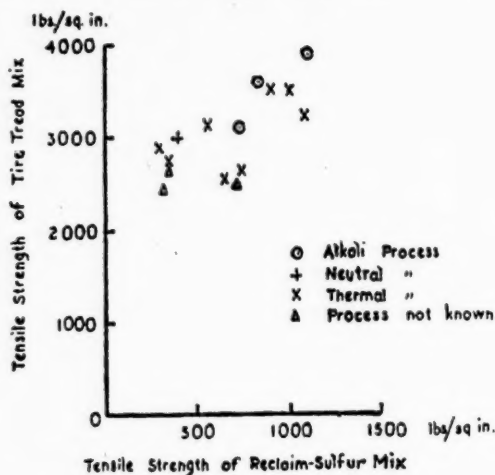


FIG. 1.

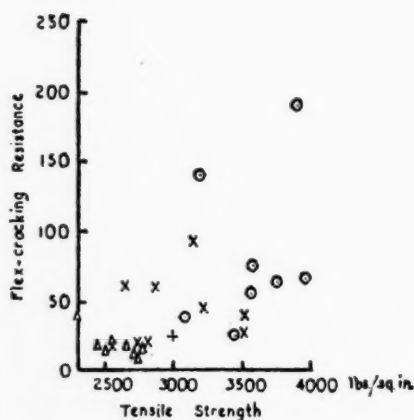


FIG. 2.

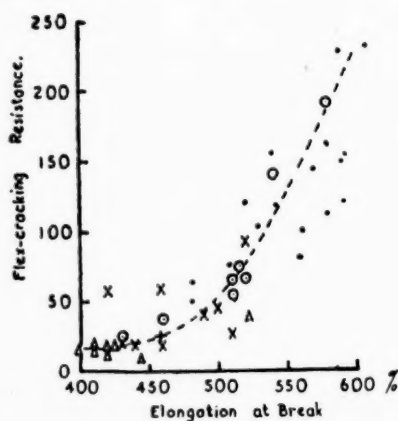


FIG. 3.

Figure 1 shows that there is a significant tendency for the same reclaim to give high (or low) tensile strengths in both types of mix. Again, however, the relationship is far from exact, since reclaims that behave alike in the simple mix may give tread stocks differing by nearly 1,000 lbs. per sq. in. in tensile strength. There is no evidence that the relation between the results for reclaim-sulfur and tire-tread mixes is different for the different types of reclaim

(alkali, neutral, thermal). It may be noted that a tread mix of similar composition but without reclaim (rubber 100, sulfur 3, channel black 50, zinc oxide 5, stearic acid 2.5, pine tar 4.5, mercaptobenzothiazole 0.8) gives a tensile strength of about 4,000 lbs. per sq. in. The reclaims thus vary widely in their effects on the strength of the tread mix; those giving best results in the reclaim-sulfur mix scarcely lower the strength of the tread mix, whereas those at the other extreme reduce it by nearly 40 per cent.

With breaking elongation, modulus, and hardness the signs of relationship between the results for the two mixes are slight, even if apparent at all. In particular, it may be noted that, with the exception of Nos. 3 and 18, all the reclaims listed in Table 2 give tread stocks with nearly the same modulus, *i.e.*, between 1,470 and 1,840 lbs. per sq. in. for M300, in spite of the very large variation in the modulus of the reclaim-sulfur mix, namely, 280 to about 1,000 lbs. per sq. in. or above. It must, therefore, be concluded that with respect for these properties, the reclaim-sulfur mix is of little or no use in predicting the behavior of a reclaim in a commercial mix.

#### ABRASION AND FLEX-CRACKING OF TIRE TREAD MIX: RELATION TO PROPERTIES OF RECLAIM-SULFUR MIX

Plotting abrasion-resistance and flex-cracking resistance of the tread mix against the various properties of the reclaim-sulfur mix shows no relationship whatever in the following cases:—abrasion-resistance and tensile strength; flex-cracking resistance and hardness; flex-cracking resistance and modulus.

Flexing plotted against tensile strength or breaking elongation shows signs of a proportionality, but far too indefinitely to make these latter properties of the reclaim-sulfur mix of any value in forecasting the flexing life of stocks in which the reclaim is used.

#### ABRASION AND FLEX-CRACKING ON THE TIRE TREAD MIX: RELATION TO OTHER PROPERTIES OF THE SAME MIX

It was thought of interest to see also whether abrasion and flexing life bore any relation to the tensile properties of the tire tread mix itself.

Some parallelism between tensile strength and abrasion-resistance might be expected, but actually none can be found in the data recorded in Table 1.

Flexing does, however, correlate with tensile properties, as will be seen from Figures 2 and 3. The relationship with breaking elongation is particularly good, as only a few points (all for nonalkali reclaims) lie far away from the curve representing the general trend. A statistical examination of the data shows, indeed, that the observed flexing-elongation relationship is much too definite to be purely accidental. Some parallelism between these properties might be expected, because the flexing test subjects all the rubbers to the same degree of stretching, which is nearer to the breaking point the lower the extensibility of the rubber. Although the extensibility is initially much greater than the stretching imposed by the flexing test, fatigue and (or) oxidation effects doubtless gradually reduce the extensibility towards the latter figure.

It is found also that, generally speaking, the flex-cracking resistance is better the softer the rubber, as indicated by the hardness or modulus, but the relationship is nothing like so close as with breaking elongation.

Among these reclaim mixes, therefore, breaking elongation appears to be the dominant factor in controlling the flexing life, irrespective of the type of reclaim present. Figure 3 shows, moreover, that a small change in elongation

has a big effect; over the range covered by these rubbers, an increase of one-tenth in breaking elongation approximately doubles the flexing life. It is possible, of course, that the relation between elongation and flexing life is not one of simple cause and effect, but that both may be determined by some third factor, so that their apparent relationship arises indirectly.

It is not claimed that the close relation between elongation and flexing is universal, since it is known that flexing life can be considerably increased, *e.g.*, by special types of antioxidant, or decreased by certain extenders<sup>15</sup>, without elongation being markedly affected. It is important to note, however, that blank tread mixes similar to those above but without reclaim (smoked sheet 100, sulfur 3, channel black 50, zinc oxide 5, stearic acid 2.5, pine tar 4.5, mercaptobenzothiazole 0.8) show substantially the same relation between flexing and elongation as do the reclaim mixes. Such blank mixes made from time to time have shown considerable variation among themselves, owing to differences in batches of raw rubber, state of vulcanization, and other factors. The results for these are included in Figure 3, and clearly tend to lie along the same curve as the points for the reclaim mixes. This shows that the use of reclaim in a tread stock does not in general markedly affect flex-cracking resistance except through its influence on the breaking elongation.

#### AGING OF RECLAIM-SULFUR VULCANIZATES

Table 2 shows that there is never much loss of tensile strength during 10 days' Geer oven aging; in most cases aging has increased the tensile strength, sometimes by over 100 per cent, but has always reduced the breaking elongation. Since the latter effect means that the cross-section of the specimen at the moment of rupture is greater after aging, it seemed that this might account for the increased strength, because such an increase would occur if the breaking stress, calculated on the stretched cross-section, remained unchanged. This view is supported by the fact that during aging the tensile strength calculated on the actual section at break remains unchanged, within the limits of experimental error, in about eight out of the seventeen cases; among the other reclaims, Nos. 2, 11, 12, and 25 show an increase and Nos. 8A, 14, 15, 18, and 26 a decrease.

The practical conclusion to be drawn is that an increase in tensile strength during oven aging of a reclaim-sulfur vulcanizate is not to be regarded as necessarily indicating a good reclaim. On the other hand, a marked fall in tensile strength would appear to be an abnormal occurrence suggestive of an inferior product. It may be noted that Palmer and Crossley<sup>10</sup> consider that aging tests on reclaim-sulfur vulcanizates are of little significance.

#### SUMMARY AND CONCLUSIONS

Literature on the value of the reclaim-sulfur test mix as a criterion of the quality of reclaim is briefly discussed, as a result of which the general conclusion is reached that such a mix is unreliable.

This point is further studied by experiments on several reclaims made by the alkali, thermal, neutral, and other processes. The tensile strengths of the reclaim-sulfur mix and of a degraded tire-tread mix (80:40 new rubber/reclaim ratio) definitely tend to run parallel, so that, for instance, a reclaim showing over 1,000 lbs. per sq. in. in the former mix would be unlikely to give a really bad tensile strength in the tread mix, and one showing 300 lbs. per sq. in., or less would be equally unlikely to give a good strength. The reclaim-sulfur mix,

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Essex  
Daw  
Newt

however, is only a rough guide, because reclaims shown to be alike by this mix may give very different properties in the tread mix.

Other properties of the reclaim-sulfur mix (breaking elongation, modulus, hardness) give no information as to the behavior of the reclaim in a tread mix; neither do the tensile properties of the former give much help in predicting how the tread mix withstands abrasion and flexing. Accelerated aging tests on reclaim-sulfur vulcanizates are of little value, except that a rapid fall in tensile strength would cast suspicion on the reclaim.

These results, emphasizing as they do the uninformative nature of reclaim-sulfur test results, suggest that, whenever possible, reclaims should be tested in the type of mix in which they are to be used, rather than in an arbitrary standard mix.

The dependence of abrasion and flexing of the tread mix on its tensile properties is examined. Abrasion-resistance is not obviously related to these properties, but flex-cracking resistance shows a parallelism with tensile strength and especially with breaking elongation. The data are consistent with the view that the latter is the dominant factor in determining flexing life, and that the substitution of reclaim for new rubber in a tread mix does not affect flexing life except through its influence on breaking elongation; it is not yet demonstrated whether elongation directly determines the flexing life, or whether both are functions of some third property.

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## THE DETERMINATION OF COPPER IN CRUDE RUBBER \*

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All types of rubber contain some copper. Although the proportion is in general extremely low, it is well not to disregard it, for this element acts as a catalyst which has a deleterious effect on the aging of rubber. For rubber to age satisfactorily it should contain not more than 1.5 mg. of copper per 100 grams of rubber; hence the interest in any method for determining the copper content of crude rubber.

### PRESENT METHOD

The method used thus far is based on the color reaction which sodium diethyldithiocarbamate gives with a very dilute copper solution. According to the method of the British Standards Institution, the ash is treated with hydrochloric acid, and the metals of the iron group are then precipitated by ammonia. After solution of the precipitate in hydrochloric acid and reprecipitation by ammonia, the filtrate is brought to the boiling point and finally is diluted to a known volume. This solution is then used for a colorimetric determination.

As a result of numerous experiments with crude rubbers from different sources in which the method described above was used, it has been found that the reagent called for in this method is not specific enough; in fact it gives a color reaction with metals other than copper, notably with iron, manganese, zinc and heavy metals which cannot be separated reliably by the ammonia method. There would seem to be two solutions to this problem; either to develop another method which employs a reagent having a more specific action, or to improve the currently used method of the British Standards Association in such a way as to eliminate the disturbing ions.

### USE OF ANOTHER REAGENT

While leaving almost unaltered the method for preparing the solution from the rubber, sodium diethyldithiocarbamate was replaced by dithiooxamide, which is an excellent reagent for copper. It was found at the start that silica is a disturbing factor and that it is a source of trouble in the analysis; accordingly it had to be rendered insoluble by treatment with hydrochloric acid, evaporation to dryness, and dissolution again in this acid. This gave more satisfactory results. However, it was still desirable to make a direct comparison of the two reagents, so determinations were made of the copper contents of two very different types of rubber, *viz.*, first-latex rubber and wild rubber from French Guiana. The following results were obtained, expressed as mg. of copper per 100 grams of crude rubber:

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 22, No. 5, pages 93-95, May 1945.

TABLE 1

Reagent	First-latex rubber	Wild rubber
Sodium diethyldithiocarbamate	0.8	30
Dithioöxamide	0.5	trace

The much higher values obtained with sodium diethyldithiocarbamate, particularly in the case of wild rubber, proved clearly the influence of foreign metals on the results obtained by the standard procedure. To make certain that the values obtained with dithioöxamide agreed closely with the true amounts of copper in the two types of rubber, a known amount of copper sulfate was incorporated in the rubber, and the latter was then analyzed. The amount of copper added to the rubber was completely recovered by analysis.

The colorations obtained with dithioöxamide were still not very sharply defined, and it seemed necessary to operate with more concentrated solutions. But these did not show exactly the same colorations as those of the corresponding pure copper solutions. Furthermore, the colorations obtained with rubber were not stable; they had a tendency to become dull and then to fade gradually.

In addition, manganese, which is present in small amounts in some types of rubber, gives a yellowish coloration with dithioöxamide. For these various reasons, it was attempted to find another means of determining copper in rubber.

#### IMPROVEMENT OF THE OLD METHOD

Using as a basis some recent experiments by Picotti and Baldassi<sup>1</sup> and by Palfrey, Hobert, Benning and Dobratz<sup>2</sup>, the older method employing sodium diethyldithiocarbamate was modified in the following way.

Disturbing metals, such as iron, aluminum, and manganese, are separated by treatment with 10 per cent disodium phosphate in ammoniacal medium at the boiling point, after treatment of the ash with hydrochloric acid and insolubilization of the silica. The mixture is filtered, the residue is washed with aqueous ammonia (1:1), the filtrate is poured into a small separatory funnel, 1 cc. of 0.1 per cent sodium diethyldithiocarbamate solution is added<sup>3</sup>, the mixture is agitated, 10 cc. of ether is added, and the mixture is again agitated. All the coloration passes into the ether and becomes clearer and more intense. The product is decanted, and the ether layer is transferred to a Nessler tube, which serves for the colorimetric determination.

Analyses by this method showed that it is sufficiently sensitive but that it has one serious inconvenience, *viz.*, that ether is too volatile to be used on plantations in the Colonies. It was necessary, therefore, to find a solvent having a higher boiling point. Various ether oxides and available esters were tried, but without satisfactory results. Finally a choice was made of isoamyl alcohol, which is a commercial product and the use of which in determining copper in the tissues of aquatic animals has already been described by Picotti and Baldassi<sup>1</sup>. Unfortunately, however, this alcohol has the drawback of a tendency to form emulsions. To overcome this fault, it was decided to heat the emulsion and to decant while hot. This proved to be a very convenient procedure, but it was still not quite satisfactory, and only by placing the colored layer of isoamyl alcohol in an oven at 110° C to eliminate all traces of water was it possible to make colorimetric comparisons which were as satisfactory and as reliable as those with ordinary ether.



Taking advantage of these modifications, determinations were made of the copper contents of 5 grams of a plantation rubber and also of the same rubber to which a known quantity of copper had been added in the form of a copper sulfate solution containing a known concentration of copper.

The differences between the experimentally determined amounts of copper and those actually added were very small.

TABLE 2

Rubber	Copper in rubber (mg.)	Copper added (mg.)	Total copper (mg.)	Copper found (mg.)	Difference (mg.)
Plantation	0.019	0.020	0.039	0.035	-0.004
Wild	0.024	0.020	0.044	0.048	+0.004
Smoked sheet	0.023	0.020	0.043	0.045	+0.002

A similar experiment was carried out with wild rubber from Guiana and with first-latex rubber, and differences of the same small order of magnitude were found.

To make certain of the reproducibility of the results, three analyses of wild rubber and of first-latex rubber were made. The results, expressed as mg. of copper per 100 grams of rubber, are shown in Table 3.

TABLE 3  
REPRODUCIBILITY OF RESULTS

Rubber	Analysis 1	Analysis 2	Analysis 3
Wild	0.48	0.47	0.47
First latex	0.47	0.51	0.48

These results show a very satisfactory reproducibility.

The sensitivity of the method for different concentrations of copper was then investigated. With 1 and 2  $\gamma$  of copper per 10 cc. of solution, *i.e.*, concentrations of  $10^{-7}$  and  $2 \times 10^{-7}$ , respectively, the two colorations, although very faint, were distinctly different. The limit of sensitivity of the reagent in this procedure seems to be about 0.5 $\gamma$ , *i.e.*, 0.05 mg. per liter or a concentration of  $5 \times 10^{-8}$ .

Table 4 gives the results obtained with higher concentrations.

TABLE 4  
SENSITIVITY OF THE COLORIMETRIC METHOD OF DETERMINATION  
AT VARIOUS CONCENTRATIONS

Concentration of two adjacent tubes	True ratio	Ratio found
0.5-0.6	1.20	1.18
1.0-1.1	1.10	1.20
1.5-1.6	1.06	1.02
2.0-2.1	1.05	1.00

These determinations were made with an ordinary Hellige prism colorimeter.

With a view to determining the part played by the operator in the results obtained by this colorimetric method, two tubes, each containing 15 $\gamma$  of copper, were prepared, and twelve people—chemists and nonchemists—were asked to compare the two colors obtained by three measurements of each. The results are shown in Table 5.

Based on the results shown in Table 5, it can be concluded that the ratios fluctuate around 1, the theoretical value; although some operators found rather divergent values, *e.g.*, 1.15 to 0.90, the mean values lie within very satisfactory limits, and are on the whole within the limits of error to be expected on a basis of the sensitivity of the method.

In conclusion, it is possible to detect by this method 0.01 mg. of copper in 100 grams of rubber, and actual quantities of copper of 0.3 mg. to 0.01 mg. The method is rapid and its precision is satisfactory. Its only inconvenience is the use of isoamyl alcohol, which necessitates working under a hood so as to avoid the noxious effects of this alcohol. Whenever the prevailing temperature makes it possible, it is more satisfactory to use ether.

TABLE 5

REPRODUCIBILITY OF COLORIMETRIC MEASUREMENTS, ACCORDING TO THE OPERATOR, OF TWO SOLUTIONS OF THE SAME CONCENTRATION

	1	2	3	4	5	6	7	8	9	10	11	12
Ratio of coloration	0.92	0.94	1.00	1.07	0.97	1.05	1.15	1.08	0.99	1.02	0.99	1.02
	0.93	0.95	1.06	0.96	0.97	1.02	0.90	0.96	1.01	0.99	1.03	1.00
	0.97	0.98	0.99	0.98	0.91	1.03	0.96	1.02	0.96	1.02	0.95	0.97
Mean value	0.94	0.96	1.02	1.00	0.95	1.03	1.00	1.02	0.99	1.01	0.99	1.00

Without a colorimeter, and using only Nessler tubes, the precision is almost as great. The use of a colorimeter, however, avoids dilution of the solution to the point at which the coloration of the two tubes to be compared is the same, and thus makes the determination more rapid.

On the basis of the experiments described above, it has been possible to develop the following procedure.

#### PROCEDURE FOR THE MICRODETERMINATION OF COPPER IN THE ASH OF RUBBER

**Principle.**—The principle of the method is the colorimetric determination of copper by sodium diethyldithiocarbamate. Disturbing metals are separated and removed hot by disodium phosphate in an ammoniacal medium. The comparison of colors is made in isoamyl alcohol free of water.

**Reagents.**—The following reagents are necessary:

Pure hydrochloric acid.

Dilute hydrochloric acid (1:3).

Pure concentrated ammonium hydroxide.

Dilute ammonium hydroxide (1:3).

Disodium phosphate (10 per cent solution).

Aqueous sodium diethyldithiocarbamate (0.1 per cent aqueous solution).

(This solution must be absolutely colorless, and a yellow bottle is recommended if it is to be kept several days.)

Isoamyl alcohol (colorless).

Standard solution of copper at  $10^{-5}$  concentration (To prepare this, dissolve 3.927 grams of pure crystalline copper sulfate in distilled water in a calibrated flask, and make up to exactly 1000 cc. Remove 10 cc. of this solution, dilute 100 times in another flask of 1000 cc. calibrated capacity. One cc. of this final solution contains 0.01 mg. of copper.)

**Analytical procedure.**—Weigh precisely approximately 5 grams of rubber sample, and incinerate it by heating at first over a small flame. It is recom-

mended that the crucible be placed on an asbestos plate with a hole in its center. When all the rubber is decomposed, place the crucible in a muffle furnace, and heat at redness until the ash is white. Do not heat over a gas burner, otherwise contamination with traces of copper is possible. Dissolve the ash in 5 cc. of pure hydrochloric acid; evaporate to dryness on a sand bath so as to render the silica insoluble; take up the residue in 5 cc. of dilute (1:3) hydrochloric acid; warm the solution, dilute to approximately twice its volume; filter, and wash with a very little distilled water.

To separate any disturbing metals, treat the filtrate with 3 cc. of concentrated ammonium hydroxide and 2 cc. of 10 per cent aqueous disodium phosphate; boil the solution several minutes to flocculate the precipitate; filter, and wash with dilute (1:3) ammonium hydroxide.

To the filtrate, reduced if necessary by evaporation to about 20 cc., add 1 cc. of reagent, agitate, add 10–12 cc. of isoamyl alcohol, agitate, heat to the boiling point (avoiding any spattering), separate the yellow-tinted isoamyl alcohol, pour it into a small separatory funnel, and collect the colored layer without delay in a crystallizing dish. Place this in an oven at 110° C until all traces of water have been eliminated, and pour the residual liquid into a 10-cc. Nessler tube. The solution should remain absolutely clear. If not, clarify it with a little isoamyl alcohol.

To prepare a series of colors as a standard scale, place 2 cc., 5 cc., 10 cc., and 20 cc. of the standard copper solution in small beakers, add to each 1 cc. of dilute (1:3) ammonium hydroxide, then add 1 cc. of reagent, agitate, add as before 10–12 cc. of isoamyl alcohol, heat, decant, heat in an oven as before, and cool.

Compare the color obtained with the sample solution to be analyzed, and dilute the standard solution which is most nearly like that of the isoamyl alcohol until the color becomes identical with that of the solution of the sample.

It is strongly recommended that a blank determination be carried out with the reagents. This will often show the need of a small correction.

The results are expressed as mg. of copper per 100 grams of rubber.

Let  $P$  be the weight (in grams) of the sample;  $N$  the number of cc. of standard solution used to obtain the same coloration as that of the sample solution being analyzed; and  $n$  the number of cc. of standard solution used to obtain the same coloration as that of the blank.

$$\text{Copper (mg. per 100 g. of rubber)} = \frac{N - n}{P}$$

Whenever the surrounding temperature makes it possible, it is more satisfactory to use ordinary ether, but it is often necessary to make two extractions to recover all the color. In addition, it is useless in this case to heat in an oven at 110° C.

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- <sup>3</sup> The 0.1 per cent solution of sodium diethylthiocarbamate keeps better in a yellow bottle. In any case, it must be replaced frequently.

# COMPARISON OF ULTRAVIOLET ABSORPTION AND CHLORINE ANALYSIS METHODS FOR COMPOSITION OF BUTADIENE-*p*-CHLOROSTYRENE COPOLYMERS \*

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The percentage of chlorine in a copolymer containing chlorostyrene can be determined by amperometric titration of the chloride ion present after sodium fusion of the polymer<sup>1</sup>. Since the percentage of chlorine is proportional to the percentage of chlorostyrene, the composition of a butadiene-chlorostyrene copolymer may be determined directly. This absolute method of composition determination affords a means of checking the ultraviolet spectrophotometric method which has been proposed for the determination of the composition of butadiene-styrene copolymers<sup>2</sup>. In the application of the spectrophotometric method it is assumed that the specific extinction coefficient of the copolymer varies linearly with the percentage of styrene between the values of the same wave length for polybutadiene and polystyrene. The spectrophotometric measurements are made at 260.0  $m\mu$  or at 269.5  $m\mu$  for copolymers of butadiene with styrene or with *p*-chlorostyrene, respectively.

TABLE I

Sample	Specific extinction at 269.5 $m\mu$	Chlorine (%)	<i>p</i> -Chlorostyrene (%)	
			Spectrophotometric method	Chlorine analysis
1	0.315	2.70	10.3	10.6
2	0.709	6.26	24.8	24.5
3	1.182	10.50	42.1	41.1

A series of butadiene-*p*-chlorostyrene copolymers was prepared by emulsion polymerization at 50° C, with various monomer ratios in the charge, to approximately 75-80 per cent conversion<sup>3</sup>. After coagulation of the latices with ethanol, the copolymers were purified by two- or threefold precipitation from chloroform with ethanol. The spectrophotometric measurements were made with the Beckman spectrophotometer, using chloroform solutions.

The results of the chlorine determinations and spectrophotometric measurements are given in Table I. In calculating the percentage of *p*-chlorostyrene from the specific extinction, the values 2.775 and 0.031 were used for the specific

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extinctions of pure poly-*p*-chlorostyrene and pure polybutadiene, respectively, at 269.5 m $\mu$ .

The results obtained by the spectrophotometric method compare well with those obtained by direct stoichiometry (the relative accuracy of the spectrophotometric method is about 3-4 per cent). This proves the correctness of the assumption that the specific extinction coefficient of the copolymer varies linearly with the percentage composition, within the limits of experimental error.

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- <sup>3</sup> The polymerization formula is given in the paper by Meehan, *J. Polymer Science* **1**, 175 (1946).

# COMPARISON OF THE BROMINE AND NITRIC ACID METHODS OF ESTIMATING SULFUR IN ACETONE EXTRACTS \*

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Dawson and Porritt<sup>1</sup> have recommended two methods for the determination of sulfur in acetone extracts. The first of these is called the bromine method, the second the nitric acid method; the former relies on bromine and water to effect the oxidation of the sulfur, while the latter uses nitric acid and potassium chlorate. There appears to be some difference of opinion as to the relative values obtained by these two methods. It has been pointed out<sup>2</sup> that the term "free sulfur" is variously interpreted as meaning either (1) the elementary sulfur extractable by boiling acetone (sometimes called "true free sulfur"), or (2) the total sulfur (elementary and combined) in the acetone extract. Of the two methods described it is stated that the bromine method gives the closer approximation to (1) and the nitric acid method the closer approximation to (2). The purpose of the present investigation was to determine whether this difference existed, whether it was of sufficient magnitude to be significant, and, if possible, to observe what factors contributed to any differences that might be observed.

The details of the two methods, as given by Dawson and Porritt, are as follows.

## (A) BROMINE METHOD

Add to the flask containing the dried acetone extract 50 cc. of distilled water and 1-3 cc. of bromine, and cover with a watch glass. If much free sulfur is present in the extract, add more bromine. Allow the flask to stand for at least 0.5 hour on a hot plate or in a water bath at about 70° C; then heat cautiously until the solution is practically colorless (do not boil). Filter the solution and precipitate the sulfate with barium chloride in the usual way.

## (B) NITRIC ACID METHOD

Add to the flask containing the dried acetone extract 30 cc. of pure concentrated nitric acid, cover with a watch glass, and heat on a steam bath for 4 hours, or, if necessary, for a longer period until most of the organic matter is destroyed. After the end of the first hour add 2.5 grams of potassium chlorate in small portions at intervals to accelerate oxidation. Evaporate the contents of the flask to dryness, add 15 cc. of concentrated hydrochloric acid, and again evaporate to dryness. Take up the residue with 50 cc. of hot distilled water and 5 cc. of dilute (2N) hydrochloric acid, filter, and make up to 250 cc. with distilled water. Precipitate the sulfate with barium chloride in the usual way.

With the previously defined objects in view these two methods were each applied to the following materials:—(1) Acetone extracts from two samples of

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ebonite; (2) Elementary sulfur; (3) Typical accelerators containing sulfur; (4) Rubber substitutes; (5) Rubber resin which had been heated with sulfur.

### 1. Acetone Extracts of Ebonite

The sulfur in dried acetone extracts obtained from two different ebonites was estimated by both methods, and the following figures (mean of duplicate tests) were obtained. Both the ebonites were rubber-sulfur mixes and only differed in their degree of vulcanization.

TABLE 1

Specimen No. of ebonite and weights of ebonite taken	Free sulfur (% on ebonite)	
	Bromine method	Nitric acid method
M1, 1.5 g.	1.76	1.73
M10, 2 g.	0.92	0.92

From these figures it is seen that as far as unloaded rubber-sulfur ebonites are concerned the two methods show good agreement, the slight difference occurring with M1 being scarcely significant.

### 2. Elementary sulfur

A sample of sublimed flowers of sulfur was chosen in preference to ground roll for this part of the work as it was probably purer. For the actual determinations about 0.05 gram (maximum amount normally present in an extract) of the sulfur was weighed out as accurately as possible in each case. The bromine method returned 98.1 per cent as sulfur and the nitric acid method 98.0 per cent. It is reasonable, therefore, to conclude from these figures that both methods are capable of giving similar results for elementary sulfur and that both are capable of oxidizing substantially all the sulfur.

### 3. Typical sulfur-bearing accelerators

The two methods were applied to a selection of typical sulfur-bearing vulcanization accelerators and the following results (mean of duplicate tests) were obtained.

TABLE 2

Accelerator, and weight taken	Theoretical sulfur content (%)	% sulfur found by	
		Bromine method	Nitric acid method
Mercaptobenzothiazole, (0.15 gram)	38.3	23.5	31.3
Tetramethylthiuram disulfide (0.12 gram)	53.0	35.9	51.5
Piperidinepentamethylene dithio- carbamate (0.2 gram)	26.0	19.5	14.8
Zinc isopropyl xanthate (0.15 gram)	35.2	19.4	22.5
Thiocarbamilide (0.25 gram)	14.3	3.1	14.0

As these accelerators were commercial products and had not been purified in any way the low figures obtained by both methods for mercaptobenzothiazole, piperidinepentamethylene dithiocarbamate, and zinc isopropyl xanthate, raised doubts as to whether the actual sulfur content really approximated to the theoretical. To settle this the total sulfur of each of these three accelerators

was determined by the Carius method and the following results, which agree reasonably well with the theoretical, were obtained.

Mercaptobenzothiazole	40.3% sulfur
Piperidinepentamethylene dithiocarbamate	25.3% sulfur
Zinc isopropyl xanthate	36.9% sulfur

Thus in not one of the five sulfur-bearing accelerators examined does the bromine method give more than approximately three-quarters of the total sulfur, in one case the figure is very low; in only two cases out of the five does the nitric acid method approach the true figure. On comparing the results obtained by the two methods, it is seen that in no instance does one method give the same result as the other, and furthermore neither can claim consistently to give the higher results, for while the nitric acid method gives the higher and more nearly correct result in four cases, in the fifth with piperidinepentamethylene dithiocarbamate the bromine method gives a definitely higher figure.

To obtain a better understanding of the significance of these differences a typical rubber mixing containing 0.75 part of accelerator per 100 of rubber, plus the usual sulfur, zinc oxide and stearic acid (total formula weight, say, 109.25) may be considered; if it be assumed that the accelerator is present in the same form after vulcanization and is completely extractable by hot acetone the actual amounts of sulfur derived from the accelerator, and the amounts returned by analysis, would be as follows.

TABLE 3

Accelerator	Theoretical amount of sulfur from accelerator (%)	Amount of sulfur that would be found by bromine (%)	Amount of sulfur that would be found by nitric acid (%)
Mercaptobenzothiazole	0.27	0.16	0.21
Tetramethylthiuram disulfide	0.36	0.25	0.35
Piperidinepentamethylene dithiocarbamate	0.18	0.13	0.10
Zinc isopropyl xanthate	0.24	0.13	0.15
Thiocarbamilide	0.02	0.02	0.10

It is evident from this table that, whereas when dealing with the accelerator itself, the difference between the two methods is usually large, when the accelerator is compounded in the normal proportion with rubber these differences become, in most cases, almost negligible. To determine the exact magnitude of the differences it would, of course, be necessary to make tests on vulcanizates containing the various accelerators.

#### 4. Rubber Substitutes

The "free" sulfur contents of a light and a dark rubber substitute were estimated by extracting the substitutes with acetone and applying the two methods to the extracts. The following results were obtained as the mean of duplicate tests.

TABLE 4

Type of substitute and weight taken	Sulfur (% on substitute)	
	Bromine method	Nitric acid method
Light substitute (1 gram)	0.33	0.35
Dark substitute (1.5 grams)	3.64	3.26

Owing to the fact that substitutes are sometimes used in rubber mixings in relatively large proportions, the difference between the two methods in the case of the dark substitute might lead to appreciably different results in the analysis of the rubber.

#### 5. Sulfur in combination with acetone-soluble resins

During the process of vulcanization, sulfur reacts with the natural resins and proteins present in the rubber to form complex sulfur compounds, some of which are acetone-soluble. To investigate this point in relation to the present work, 200 grams of pale crêpe were extracted with acetone, 0.25 grams of sulfur was added to the liquid extract, the acetone was distilled off, and the residue was heated for 4 hours at 140° C. After this treatment a portion of the material (which consisted of a dark brown viscous liquid with a high surface gloss), was extracted with acetone to ascertain whether the "vulcanizing" treatment had rendered any of the previously soluble resins insoluble, but it was found that the material had not changed in this respect, and was completely extractable with acetone. The total sulfur present was determined by the Carius method and the results so obtained were compared with those given by the two methods under investigation. Mean results of duplicate tests, using about 0.4 gram of the "vulcanized" resin in each test, are given below.

TABLE 5  
SULFUR CONTENT OF "VULCANIZED" RESIN

Total sulfur by Carius	Sulfur by bromine method	Sulfur by nitric acid method
4.46%	1.55%	3.46%

If it is assumed that the bromine method at least oxidizes all the free sulfur, it is evident that the nitric acid method attacks a considerable proportion of the sulfur combined with the resin. Although the differences between the figures here are appreciable, when the actual effects on the apparent sulfur content of the acetone extract of a vulcanized rubber are calculated, the magnitude of the differences is seen in better perspective from the point of view of this investigation. Using the mixing previously quoted, but omitting the accelerator, the difference between the results obtained by the two methods only amounts to 0.05 per cent. Nevertheless, since the difference in the case of mercapto-benzothiazole is in the same direction, if this accelerator be included in the mix a total difference of 0.10 per cent is produced, and this may well be of some significance in certain circumstances.

#### CONCLUSION

From the experiments described, it appears that neither the bromine method nor the nitric acid method is perfectly satisfactory, for the following reasons.

(1) Neither method gives the true free sulfur in rubbers containing sulfur-bearing accelerators, as these cause positive errors of anything up to 0.2-0.3 per cent.

(2) The nitric acid method does not give the true free sulfur in rubbers, without sulfur-bearing accelerators, because the result includes some of the

sulfur combined with the rubber "resins"; the tests do not show definitely whether this applies also to the bromine method.

(3) Neither method gives the total sulfur in the acetone extract, since some of the sulfur combined with the "resins" is not included in the result; the presence of certain sulfur-bearing accelerators increases the error.

The statement previously referred to (*loc. cit.*), that the bromine method approximates more nearly to the elementary sulfur content and the nitric acid method more nearly to the total sulfur content of the extract, appears to be a correct generalization. In most cases, however, the difference between the results obtained by the two methods would be less than 0.1 per cent.

In respect of simplicity and rapidity of working, the bromine method has the advantage over the nitric acid method, and therefore in all ordinary circumstances is the one to be recommended.

#### REFERENCES

- <sup>1</sup> Dawson and Porritt, "Rubber: Physical and Chemical Properties", Research Assoc. Brit. Rubber Manufacturers, Croydon, 1935, p. 535.
- <sup>2</sup> Dawson and Porritt, "Rubber: Physical and Chemical Properties", Research Assoc. Brit. Rubber Manufacturers, Croydon, 1935, p. 532.

## DETERMINATION OF RUBBER HYDROCARBON BY A GRAVIMETRIC RUBBER BROMIDE METHOD \*

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Direct determination of rubber hydrocarbon in crude rubbers and in latices has been generally considered so inaccurate and unreliable that determination of rubber hydrocarbon by difference has been a common practice. The difference method usually suffices in the analysis of products derived from Hevea rubber, in which the nonrubber components have been well characterized or occur in low concentration. In the analysis of natural rubber products obtained from sources other than Hevea, such as guayule, kok-saghyz, and *Cryptostegia*, the situation is different. The chemical and physical properties of the nonrubber components of such products are largely unknown, and in many cases the nonrubber contaminants are present in excessive amounts, sometimes more than 50 per cent of the total. Since the rubber hydrocarbon analysis usually affords the most reliable means for estimating the rubber content of plants and for following the concentration and purification of rubber by mechanical and chemical processes, it appeared desirable to devise or adapt a method which would permit direct determination of this constituent in the presence of relatively large amounts of natural and added contaminants.

Among the methods for determination of rubber in the literature, those which have received the largest amount of study are the gravimetric<sup>1</sup> and volumetric<sup>2</sup> methods based on the formation of the bromine derivative of rubber. Other methods are the empirical chromic acid oxidation<sup>3</sup>, the direct alcohol precipitation<sup>4</sup>, and the nitrosite procedures<sup>5</sup>. The gravimetric bromide method showed the greatest promise of adaptability to the determination of rubber hydrocarbon in a wide variety of products containing rubber. Both the volumetric bromide method and the chromic acid oxidation method are subject to error when the rubber contains material other than rubber hydrocarbon, since any nonrubber compounds capable of reacting with bromine interfere in the volumetric bromide method and any components yielding volatile acids on digestion with chromic acid tend to give high results if the chromic acid oxidation method is employed. Estimation of rubber by direct weighing of the hydrocarbon precipitated with alcohol is not applicable to the determination of rubber in impure or dilute solutions. The nitrosite method was not investigated, since it has never met with favor because of the uncertain composition of the reaction products. The gravimetric bromide method was therefore selected for further investigation as a possible and practical means for the direct estimation of rubber hydrocarbon.

The bromine derivative of rubber or the so-called "tetrabromide" was first prepared by Gladstone and Hibbert<sup>6</sup>, who isolated the compound by evaporating the solvent from a chloroform-rubber solution that had been treated with

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bromine. Weber<sup>7</sup> found that the compound could be more conveniently isolated by precipitation with alcohol. Analysis of his preparation showed a composition in essential agreement with the formula,  $C_{10}H_{16}Br_4$ . The methods devised for determination of rubber hydrocarbon based on the formation of the bromide vary in the choice of (1) rubber solvent (carbon tetrachloride, chloroform, or benzene), (2) brominating conditions, such as time, temperature, and composition and concentration of the reagent, and (3) bromide precipitant (alcohol, acetone, or petroleum ether). In several of the methods the bromine, in the isolated bromide precipitate is determined and the amount of rubber hydrocarbon calculated by using the ratio of 1 isoprene unit ( $C_5H_8$ ) to 2 bromine.

Several early investigators recognized that this theoretical ratio was not obtained in practice, since formation of the bromide was generally accompanied by liberation of hydrogen bromide, indicating that substitution as well as addition of bromine took place. Hinrichsen and Kindischer<sup>8</sup> observed no liberation of hydrogen bromide if the bromination was carried out at  $0^\circ C$ , and proposed a method based on this finding. The volumetric bromide method of Lewis and McAdams<sup>9</sup> attempted to evaluate the amount of substitution by titration of the liberated hydrogen bromide and corrected the results accordingly. Bloomfield<sup>10</sup> has recently reported that when bromination of rubber is carried out at temperatures below  $0^\circ C$  in a medium containing a trace of alcohol, substitution of bromine is minimized. A simple adaptation of the bromide method was made by Edison<sup>11</sup> and his associates for use in their survey of native American plants as potential sources of natural rubber. In this method, a benzene or carbon tetrachloride solution of rubber is brominated for one hour, the bromide is precipitated with alcohol, washed, dried, and weighed, and the rubber hydrocarbon content is calculated by multiplying the weight of recovered bromide by an empirical factor, 0.285, instead of the theoretical factor, 0.299.

Since conversion of weight of rubber bromide to weight of rubber is based on an empirical factor, it was necessary to establish this factor for rubber from different sources. Effects of variations in conditions were studied to determine the limits within which it is possible to use the established factor.

#### EXPERIMENTAL

Samples of rubber bromide for ultimate analysis were prepared by the bromination of benzene solutions of rubber derived from various *Cryptostegia*, *guayule*, and *kok-saghyz* products. Benzene solutions of the rubber of each plant species were obtained as benzene extracts of the acetone-extracted plant tissues, solutions of the resin-containing crude rubber, milled, or extracted from the plants, or extracts of latices or plant liquors prepared from the plants.

Accurately measured volumes of such rubber solutions containing between 2 and 2.5 mg. of rubber per cc. were brominated at room temperature by adding 1 cc. of the brominating solution (see reagents) for every 10 cc. of rubber solution. Bromination was stopped and the bromide precipitated at the end of an hour by the addition of 30 cc. of absolute alcohol for every 10 cc. of the brominated mixture. The bromide was allowed to settle for 2 hours and was then filtered, washed with absolute alcohol, and dried to constant weight at  $50^\circ C$  in *vacuo*. The dried precipitates were analyzed for carbon and hydrogen and in some cases for bromine. When the bromide was separated by filtration from the mother liquor immediately after precipitation, the weight and composition of



the recovered bromide were the same as those of the bromide separated after standing for 2 hours.

All analyses of carbon, hydrogen, and bromine were made by common microprocedures. Many analyses were made of bromides prepared from resin-free solvent-extracted rubber, crude rubber, and rubber latex obtained from each of the three plant sources. The average values in Table I were obtained by three to eight determinations of bromides from each source.

TABLE I  
COMPOSITION OF RUBBER BROMIDES \* FROM THREE PLANT SOURCES

Plant Source	Product from Which Prepared	Bromine (%)	Carbon (%)	Hydrogen (%)	Sum of C + H (%)	Total (%)
Guayule	Latex dispersion	..	25.9	3.4	29.3	..
	Crude rubber	..	25.3	3.5	28.8	..
	Acetone-extracted plant tissue	69.8	25.9	3.5	29.4	99.2
	Average		25.7	3.5	29.2	
Kok-saghyz	Crude rubber	69.9	25.7	3.2	28.9	98.8
	Acetone-extracted plant tissue	70.4	25.9	3.3	29.2	99.6
	Average		25.8	3.2	29.0	
Cryptostegia	Crude rubber	69.2	27.0	3.4	30.4	99.6
	Acetone-extracted plant tissue	69.9	26.9	3.4	30.3	100.2
	Average		26.9	3.4	30.3	
Theoretical composition of $C_6H_5Br_2$		70.12	26.34	3.54	29.88	

\* Each value is average of values obtained in three to eight determinations.

The sums of the averages of the carbon and hydrogen content give the factors for converting weights of rubber bromides to weights of rubber. The factors obtained are as follows:

Guayule	0.292
Kok-saghyz	0.290
Cryptostegia	0.303

A mean deviation of  $\pm 0.003$  for each of the three factors was obtained when the carbon and hydrogen data for all the samples were analyzed. In general usage it is not necessary to employ the two factors, 0.292 and 0.290, for guayule and kok-saghyz, respectively, but rather to use the average factor, 0.291, whose mean deviation is within the limits of experimental error.

As an additional test of the variation of the gravimetric factor for rubber in rubber bromide, many of the benzene-rubber extracts obtained in the course of plant analyses were analyzed for rubber both by the bromination procedure and by weighing the rubber film obtained by evaporation. Ultimate analyses showed that the films were 98 to 99 per cent pure. The gravimetric factors were determined by dividing the weight of the rubber film by the weight of the rubber bromide. The average of more than one hundred such determinations yielded the following factors: guayule,  $0.292 \pm 0.003$ ; kok-saghyz,  $0.290 \pm 0.004$ ; and Cryptostegia,  $0.302 \pm 0.003$ . All are in close agreement with the values obtained by the ultimate analysis of the bromides (Table I). Preliminary experiments have indicated that this method is applicable to Hevea and that the factor 0.291 gives satisfactory results. In addition, test analyses

of a sample of GR-S synthetic rubber indicated that reliable results are obtainable using an experimentally found factor of 0.342.

To evaluate variations in time, temperature, rubber concentration, and bromine concentration which would not significantly alter the factor, the weights of bromide recovered from aliquots of rubber-benzene solutions brominated under various conditions were compared. Table II shows the effect of varying the volume ratio of the brominating solution to the rubber-benzene solution.

TABLE II  
EFFECT OF VOLUME RATIO OF BROMINATING REAGENT TO RUBBER-BENZENE SOLUTION ON WEIGHT OF RUBBER PRECIPITATED

Br solution per 10 cc. of rubber-benzene solution (cc.)	Kok-saghyz		Guayule	
	Rubber bromide from 20 cc. of rubber-benzene (grams)	Wt. of rubber calculated* (grams)	Rubber bromide from 20 cc. of rubber-benzene (grams)	Wt. of rubber calculated† (grams)
1	0.1133	0.0329	0.1327	0.0387
2	0.1124	0.0326	0.1345	0.0393
3	0.1135	0.0329	0.1348	0.0394
4	0.1145	0.0332	0.1355	0.0396
5	0.1159	0.0336	0.1350	0.0394
6	0.1143	0.0331	0.1363	0.0398

\* Gravimetric factor 0.290.

† Gravimetric factor 0.292.

Although there is a slight increase in the weight of rubber bromide formed with increased amounts of the brominating solution, the weights of rubber, calculated by the factor previously established by ultimate analyses, are fairly constant. Since the variation caused by increasing amounts of brominating reagent is small, the procedure adopted has been to use 1 cc. of reagent for every 10 cc. of rubber-benzene solution, as the gravimetric factors have been established on the basis of this ratio. To change the ratio would necessitate establishing new factors which would be even further from the theoretical value of 0.299.

To show the effect of varying rubber concentration on the amounts of rubber calculated from the bromide with the established factor, a series of 10-cc. aliquots of a rubber-benzene solution was diluted with different amounts of benzene. These were brominated by the addition of 1 cc. of brominating solution for every 10 cc. of the rubber-benzene solutions. Table III shows the results.

It is evident that rubber-benzene solutions containing 0.5 to 3.0 mg. of rubber per cc. of solution can be analyzed by this procedure, with a recovery of 98 to 100 per cent. For solutions containing much more than 3.0 mg. of rubber per cc., low values were obtained.

Aliquots of benzene solutions of rubber from three plant sources were brominated at room temperature ( $25^{\circ} \pm 2.5^{\circ} \text{C}$ ) and in a refrigerator at  $4^{\circ} \text{C}$  for periods ranging from 1 to 24 hours. One milliliter of brominating reagent was used for every 10 cc. of rubber-benzene solution. Table IV shows the results.

The data indicate that reasonable variations in time and temperature of bromination from the one hour and room temperature of the described procedure cause insignificant changes in the amounts of rubber calculated from the

bromides. However, prolonged bromination at room temperature results in a gradual increase in the weight of the precipitate; this is presumably due to substitution of bromine. At 4° C the same phenomenon occurs, but, as would be expected, the rate is slower. When brominations were made at -4° C in carbon tetrachloride solution containing a trace of alcohol, the gravimetric factors calculated for rubber in rubber bromide formed approached the theoretical value. The proposed method of brominating at room temperature is preferred, however, because of its ease of operation, its adaptability, and the accuracy obtainable.

TABLE III  
ANALYSIS OF SOLUTIONS OF DIFFERENT RUBBER CONCENTRATIONS

Guayule			Kok-saghyz			Cryptostegia		
Mg. of rubber per 10 cc. of rubber-benzene solution		% Recovery	Mg. of rubber per 10 cc. of rubber-benzene solution		% Recovery	Mg. of rubber per 10 cc. of rubber-benzene solution		% Recovery
Added	Found*		Added	Found*		Added	Found*	
6.6	6.6	100	5.6	5.6	100	5.4	5.4	100
7.9	7.8	99	6.6	6.6	100	6.5	6.5	100
9.9	9.7	98	8.2	8.2	100	8.2	8.1	99
13.2	13.1	99	10.9	10.7	98	10.9	10.8	99
19.8	19.6	99	16.4	16.4	100	16.3	16.1	99
29.7	29.5	99	24.6	24.5	100	24.5	23.9	98
39.5	37.4	95	32.8	31.9	97	32.6	31.5	97

\* Gravimetric factors: guayule, 0.292, kok-saghyz, 0.290; Cryptostegia, 0.303. 1 cc. of brominating reagent added for each 10 cc. of rubber-benzene solution.

TABLE IV  
EFFECT OF TIME AND TEMPERATURE OF BROMINATION ON  
WEIGHT OF RUBBER FOUND

Time of Bromination (hours)	Weight of rubber calculated* from bromide precipitated from 20 cc. of solution					
	Cryptostegia		Kok-saghyz		Guayule	
	Room temp. (gram)	4° C (gram)	Room temp. (gram)	4° C (gram)	Room temp. (gram)	4° C (gram)
1	0.0162	0.0162	0.0276	0.0271	0.0405	0.0402
3	0.0164	0.0166	0.0282	0.0275	0.0418	0.0408
6	0.0178	0.0172	0.0284	0.0277	0.0427	0.0414
24	0.0184	0.0177	0.0285	0.0278	0.0442	0.0427

\* Previously established factors for bromination at room temperature for 1 hour were used.

Results of the carbon and hydrogen analyses of the bromides indicate that the gravimetric factors for converting weights of bromide to weights of rubber vary from one plant source to another. The cause of these variations has not been determined; they may be due to the inherent nature of the rubbers. That the bromide method accounts for all the rubber in a solution is indicated by the close agreement between the weights of rubber calculated by these gravimetric factors and the weights obtained by evaporation of the pure rubber benzene extracts. This agreement does not preclude the possibility of obtaining high rubber values by the bromide method from impure benzene extracts. However, the possibility is remote that any nonrubber plant materials are present which are soluble in benzene and also form alcohol-insoluble bromine derivatives. Added antioxidants and solution aids have never interfered.

## REAGENTS

Alcohol, A.C.S., absolute  
Acetone, A.C.S., analytical reagent grade  
Benzene, A.C.S., analytical reagent grade  
Trichloroacetic acid, Eastman Kodak Company White Label  
Benzene containing 1% trichloroacetic acid  
Brominating solution. Dissolve 2 grams of iodine in 100 cc. of carbon tetrachloride, filter through filter paper, and add 5 cc. of bromine to the filtrate.

## ANALYTICAL PROCEDURES

Determination of rubber by the bromide method is useful in evaluating the rubber content of benzene extracts of plant tissues, crude rubbers isolated from plants by mechanical or chemical means, and rubber-containing liquors and latices.

*Determination of Rubber in the Organic Solvent Extract of Plant Tissue.*—An organic solvent extract or the rubber film obtained by evaporating an extract may be analyzed by the bromide procedure.

To analyze a rubber film, redissolve it in benzene by stirring and gentle heating, cool, and make to volume in a volumetric flask with benzene. Choose as the final volume of either the extract or the redissolved film one which will contain 0.5 to 3.0 mg. of rubber per cc. Transfer to a beaker an aliquot containing a minimum of 25 mg. of rubber, and add 1 cc. of the brominating solution for each 10 cc. of the aliquot. Cover the beaker with a watch glass and let stand at room temperature for one hour to permit agglomeration of the particles. At the end of the hour stir the brominated mixture thoroughly with a glass rod, taking special care to loosen any precipitate from the bottom of the beaker. Add absolute alcohol, with constant stirring, in the ratio of 30 cc. of alcohol for each 10 cc. of the brominated mixture. Allow the bromide precipitate to settle for at least one hour and then filter with suction, using a tared Gooch crucible with asbestos pad. An ordinary rubber policeman and alcohol may be used in transferring the bromide and in washing the beaker. Wash the bromide several times with alcohol, dry at 50° C in vacuo under 5-mm. mercury pressure, cool, and weigh. Calculate the rubber content from the weight of the rubber bromide by the following gravimetric factors: 0.290 for kok-saghyz, 0.292 for guayule, and 0.303 for *Cryptostegia*.

*Determination of Rubber in Rubber Crudes.*—Prepare the analytical sample of the crude rubber by passing it several times through compounding rolls, finally mill it into a thin ribbonlike sheet, and from this cut or tear narrow strips for moisture and for rubber analysis.

Determine the moisture by drying approximately 2 grams of the crude rubber in vacuo at 50° C to constant weight (12 hours).

Solution of the sample for rubber analysis may be obtained either by heating it in benzene or by allowing it to stand at room temperature in a 1% solution of trichloroacetic acid in benzene. Although the latter method requires 2 to 3 days for solution, it is more convenient in routine analysis, and in general less time-consuming. Since determination of the benzene-insoluble and acetone-insoluble content of the crude rubber is usually required in addition to rubber hydrocarbon, samples of approximately 0.5 grams are recommended.

Cut or tear approximately 0.5 gram of the milled sheet into fine strips, weight to the nearest 0.1 mg., and place in a tared 70-cc. centrifuge tube. Add 50 cc. of a 1% solution of trichloroacetic acid in benzene, insert a glass

stirring rod, lightly stopper the tube with a plug of cotton, and allow it to stand at room temperature for 3 days. To aid in the complete solution of the rubber, stir two or three times a day during the 3-day interval. Centrifuge to separate the benzene-insolubles and decant the benzene-rubber solution into a 200-cc. volumetric flask. Wash the benzene-insolubles and the centrifuge tube twice with 50-cc. portions of benzene, centrifuging after each wash. Add the benzene washes to the benzene-rubber solution and dilute to 200 cc. with benzene. Determine the rubber in a 20-cc. portion of this solution by the bromide method described in the previous section. Calculate the per cent rubber in the crude by the equation:

$$\% \text{ rubber} = \frac{\text{gravimetric factor} \times \text{weight of bromide (g.)} \times \text{volume of sample (200 cc.)} \times 100}{\text{weight of crude rubber (grams)} \times \frac{100 - \% \text{ moisture}}{100} \times \text{portion used (20 cc.)}}$$

If the percentage of acetone-soluble or resin fraction and the percentage of those materials insoluble in both acetone and benzene are desired, determine the insolubles directly and calculate the acetone-solubles by difference. To determine the insoluble fraction, thoroughly wash the benzene-insoluble residue left in the centrifuge tube with acetone, separate the insolubles by centrifuging, and discard the acetone wash solution. Dry the residue in the tared centrifuge tube for one hour at 110° C in an air oven, cool, weigh, and calculate the per cent insolubles on a moisture-free basis.

TABLE V  
ANALYSES OF CRUDE RUBBER FROM DIFFERENT PLANTS

Plant source	Sample no.	% Rubber		% Insolubles (benzene and acetone)		Acetone-solubles* (resins)
Guayule	5293	65.0	65.1	15.3	15.3	19.7
	5319	78.6	79.2	5.3	5.3	15.9
	5341	68.2	68.0	10.4	10.3	21.6
	5564	73.8	73.9	7.2	7.3	18.9
	5568	77.4	77.5	1.8	1.8	20.8
Kok-saghyz	7510	80.9	80.9	6.4	6.9	12.5
	7520	86.2	86.1	7.2	7.2	6.7
	7579	77.3	76.8	8.0	8.0	15.0
	8088	79.0	78.7	7.1	7.4	13.9
	8227	77.5	77.5	9.7	9.9	12.7
Cryptostegia	7726	64.5	65.3	1.1	1.0	34.1
	9040	87.4	87.2	5.2	5.3	7.5
	9050	63.1	63.3	28.1	28.1	8.7
	9054	51.3	51.2	40.5	40.3	8.4
	9060	84.6	84.4	5.4	5.3	10.2

\* Calculated by difference from average of both rubber and insolubles.

The percentage acetone-soluble fraction is obtained by subtracting the sum of the percentages of moisture-free rubber and insolubles from 100. Since the proposed method is especially suited to the analysis of crude rubber and is applicable to samples containing either large or small amounts of nonrubber nonresin materials, several typical analyses of samples of such rubber from different plants are given in Table V. These show the reproducibility of the method.



*Determination of Rubber in Aqueous Liquors Low in Rubber Content.*—Many types of aqueous rubber-containing emulsions having rubber contents ranging from less than 1 to about 5 per cent may be conveniently analyzed for rubber by the bromide procedure. Benzene extracts of the rubber in such emulsions are most easily prepared in the Waring Blendor. The persistent emulsions which result when alkali-stabilized rubber liquors are extracted with benzene in the Blendor can be avoided by acidifying the liquor with concentrated hydrochloric acid preliminary to the extraction.

To determine the rubber content, transfer 10 to 50 cc. of the emulsion to a Waring Blendor using a transfer pipet, rinse the pipet several times with water, and combine the rinses with the measured sample, making a total volume of approximately 75 cc. Add sufficient concentrated hydrochloric acid to break the emulsion; usually 5 to 10 cc. are required. Then add about 180 cc. of benzene, churn for 2 minutes, wash the emulsion into a 500-cc. separatory funnel with water, and allow to stand until the aqueous layer appears clear, usually about 8 hours. Draw off and discard the clear aqueous layer.

Transfer the benzene and the interface layers to centrifuge tubes, centrifuge until separation into layers is complete, and transfer the benzene layer to a 400-cc. beaker using a pipet and suction. Rinse the separatory funnel with benzene. Add the rinses to the aqueous residue in the centrifuge tube, mix well, and centrifuge. Again draw off the benzene layer and add it to the original benzene solution in the beaker. Concentrate on a steam bath, transfer, and make to the mark in a volumetric flask of such volume that 20 cc. of the final volume will contain between 10 and 60 mg. of rubber. Transfer a 20-cc. aliquot to a 250-cc. beaker and brominate by the previously described procedure. Should the 20-cc. aliquot of the original solution contain more than 60 mg. of rubber, dilute to the desired concentration and brominate a 20-cc. portion. When the total benzene extract is very low in rubber, it may be reduced to 20 cc. and brominated in its entirety. Calculate the rubber content from the equation:

$$\text{Mg. of rubber per cc.} = \frac{\text{gravimetric factor} \times \text{weight of bromide (mg.)} \times \text{dilution factor}}{\text{cc. of sample}}$$

*Determination of Rubber in Latex or Liquor of High Rubber Content.*—When concentrated rubber liquors (containing more than 5 per cent rubber) and latices are being analyzed, complete extraction of the rubber by benzene cannot be achieved by the Waring Blendor method described above. Instead, benzene is added to the sample, the mixture is acidified, and the water is removed by distillation in a Bidwell-Sterling type moisture apparatus. This results in a water-free solution of the rubber in benzene.

Weigh by difference from a glass-stoppered vial that amount of the well-mixed sample which contains less than 1.5 grams of rubber and transfer to a 500-cc. volumetric (boiling) flask equipped with a 24/40ST outer joint. Acidify the sample with concentrated hydrochloric acid to give an acid concentration of about 10%, then add 200 cc. of benzene and attach the flask to a Barrett type Bidwell-Sterling moisture test apparatus provided with a condenser. Boil the mixture until all water is removed (water level in the trap remains constant), and a clear benzene solution is obtained. Remove the flask from the apparatus, cool, and dilute to the mark with benzene. Transfer, with a pipet, a 50-cc.



aliquot to a 600-cc. beaker and determine the rubber in this aliquot by the bromide method and the following equation:

$$\% \text{ rubber} = \frac{\text{Gravimetric factor} \times \text{weight of bromide (grams)} \times \text{volume of sample (500 cc.)} \times 100}{\text{weight of sample} \times \text{aliquot (50 cc.)}}$$

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# EFFECT OF BUFFING IN PREPARING DUMB-BELL TENSILE SPECIMENS \*

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## INTRODUCTION

In making tensile tests on many finished rubber articles, *e.g.*, tires, hose, conveyer belting, and soles, it is necessary to buff down the rubber or the dumb-bell specimens cut from it to obtain test-pieces of suitable and uniform thickness. The nature of the surface produced by buffing would be expected to influence the tensile test result. Moreover, buffing might cause temporary changes in the properties of the rubber, which would be eliminated only after a certain rest period.

To determine whether these effects are large, experiments have been made by buffing the rubber in various ways and by testing buffed samples at various intervals after buffing. The first series of tests were made without any special appliances for holding the rubber during buffing, but it soon became evident that for any systematic work on the subject it would be necessary to construct a machine in which buffing could be carried out under various controlled conditions. Such a machine is described in the appendix to this report.

## EXPERIMENTAL

All the experiments were made with dumb-bell specimens having  $1 \times \frac{1}{4}$  inch test-length and  $1\frac{1}{2}$  inch wide ends<sup>1</sup>. These were cut parallel to the calender grain of the rubber and tested on the Scott tensile-testing machine, of which the lower grip travelled at 20 inches per minute. For each test 4 dumb-bells were used, and the results were averaged after excluding any obviously faulty ones. In the tabulated results TS denotes tensile strength (lbs. per sq. in.), EB the breaking elongation (percentage), and M100 (300, 500, 700) the modulus (lbs. per sq. in.) at 100 (300, 500, 700) per cent elongation.

### 1. INFLUENCE OF FINENESS OF ABRASIVE WHEEL USED FOR BUFFING

Rubbers of the following compositions were examined:

	A	B
Smoked sheet	100	100
Sulfur	3	3.1
Gas black	—	38
Zinc oxide	5	7.6
Pine tar	—	3.1
Stearic acid	1	—
Diphenylguanidine	0.75	1.15

Each rubber was vulcanized in a platen press in moulds 10 inches square, giving sheets 0.2 inch thick. Two sheets were vulcanized for each of three

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periods, as follows: A: 30, 35, and 40 minutes at 153° C; B: 45, 50, and 55 minutes at 148° C.

Eight dumb-bell specimens were cut from each sheet and the sixteen specimens from each pair of sheets were then divided into four sets of four, each set containing two from each sheet.

Buffing was carried out by four different methods, using one set of four dumb-bells for each method. The dumb-bell was held by hand against a wood backing and pressed against a fused alumina grinding wheel 7 inches in diameter rotating at 1400 r.p.m. The thickness of the specimen was reduced in this way to 3 mm., care being taken to avoid overheating. The bulk of the rubber was removed with a coarse-grained wheel (36 grit). If the specimen was to be left rough, buffing was continued with this down to the final thickness. When the rubber was to be made smooth, the buffing was finished with a finer wheel (80 grit). With the carbon black rubber it was found that the coarse wheel gave a relatively smooth surface not very different from that given by the fine wheel. On the 50-minute and 55-minute vulcanizates of this rubber, therefore, a rough surface was obtained by using a cylindrical rasp 1 inch diameter, having 16 diagonal ribs per inch, rotating at 1400 r.p.m. This gave a similar surface to that obtained with the coarse corundum wheel on the soft rubber A.

The four sets of dumb-bells were treated as follows: (1) one side only buffed and finished as smooth as possible; (2) one side only buffed and surface left rough; (3) both sides buffed and finished smooth; (4) both sides buffed and left rough.

The specimens were left overnight after being buffed and then subjected to tensile tests. Results are given in Tables 1 and 2.

TABLE 1

## MIXING A

Manner of buffing	TS	EB	M300	M500	M700
<b>30 min. vulcanization</b>					
(1) one side smooth	2875	740	240	595	2275
(2) one side rough	2700	725	275	630	2380
(3) both sides smooth	2555	730	225	560	2150
(4) both sides rough	2465	715	220	555	2160
<b>35 min. vulcanization</b>					
(1) one side smooth	3150	710	290	785	3040
(2) one side rough	2940	690	290	780	—
(3) both sides smooth	3050	710	275	765	2980
(4) both sides rough	2810	695	260	740	—
<b>40 min. vulcanization</b>					
(1) one side smooth	3245	720	240	780	3020
(2) one side rough	3145	710	290	820	3100
(3) both sides smooth	3000	710	250	775	2810
(4) both sides rough	2860	690	265	780	—

Considering first the results for the "pure" mixing A, it will be seen that tensile strength is markedly affected by the manner of buffing, the variation amounting to 10–15 per cent. The general tendency is for the strength to decrease in the order (1), (2), (3), (4). As would be expected, the rough surface gives a lower result than the smooth surface, and buffing both sides gives a lower result than buffing one side. Similar, though smaller, differences are generally noticeable with the breaking elongations also.

Modulus appears to be affected to quite a marked degree by the method of buffing. Although the four methods do not fall in the same order in every case, there is a tendency for (2) to give the highest values and (3) and (4) the lowest.

With the carbon-black mixing B, the 45-minute vulcanizate, for which the coarse grinding wheel was used to obtain the "rough" surface, shows little variation in tensile strength according to the method of buffing. When, however, the rasp is used to give a rough surface similar to that obtained on mixing A, both tensile strength and breaking elongation are usually affected in much the same way and to the same extent as with the latter.

TABLE 2  
MIXING B

Manner of buffing	TS	EB	M100	M300	M500
<i>45 min. vulcanization</i>					
(1) one side smooth	3940	500	255	1740	3940
(2) one side rough	3970	515	300	1660	3805
(3) both sides smooth	4020	520	255	1740	3910
(4) both sides rough	3890	520	230	1610	3710
<i>50 min. vulcanization</i>					
(1) one side smooth	4120	525	283	1820	3945
(2) one side rough*	3950	505	278	1670	3830
(3) both sides smooth	4160	515	275	1870	4045
(4) both sides rough*	3675	505	255	1770	3690
<i>55 min. vulcanization</i>					
(1) one side smooth	4270	505	345	2030	4220
(2) one side rough*	3930	480	325	1920	—
(3) both sides smooth	4135	490	325	2060	—
(4) both sides rough*	3678	475	285	1880	—

\* Rough surface obtained by rasping on a rotating steel rasp.

Modulus is again noticeably affected, rough buffing giving in most cases lower values than smooth buffing.

At first sight it might appear that modulus should not be affected by the manner in which the specimen is buffed. There are, however, two possible ways in which this might occur.

- (1) If the surface is rough, the contact members of the usual type of thickness gauge exerting a light pressure will rest on the projections, so that the measured thickness will be greater than the mean thickness that determines the load-elongation relationship of the specimen. Rigidities calculated from the measured thickness will, therefore, be too low.
- (2) When a dumb-bell is cut from a sheet having a thickness comparable with the width of the dumb-bell, the cross-section is not rectangular and the widths at the top and the bottom are not equal<sup>2</sup>. If the thickness is then reduced the final mean width of the specimen will depend on whether the wide or narrow side has been buffed away. If, as is usual, the width of the specimen is assumed to be constant, different tests results are obtained in the two cases.

It appears from these tests that the manner in which a dumb-bell specimen is buffed can affect the measured tensile strength by as much as 10-15 per cent, the strength being reduced by leaving the surface rough or by buffing both sides instead of one. This effect is more likely to be serious with a soft rubber than with a relatively stiff one.

Breaking elongation is affected similarly but to a smaller extent. Modulus appears to be affected also, though not in a consistent manner.

These results emphasize the need, with test-pieces that have to be buffed before being subjected to tensile tests, of obtaining the smoothest possible surface by using a fine-grained abrasive.

## 2. INFLUENCE OF RATE OF BUFFING

The main object of this series of tests was to examine the influence of varying the thickness of rubber taken off at each passage over the buffing wheel, the total time during which the rubber is in contact with the wheel being kept constant.

To provide the large supply of uniform rubber needed, the rubber covering of a piece of wide conveyer belting was used. For each dumb-bell specimen a piece  $7 \times 1\frac{1}{2}$  inches was cut from the belt, with its long dimension parallel to

TABLE 3

Method of buffing		TS	EB	M100	M300	M500
A	I	3080	550	165	1050	2580
	II	2905	530	190	1100	2635
	Mean	2990	540	180	1075	2610
B	I	3000	560	175	1035	2525
	II	3020*	540*	240	1075	2620
	Mean	3010	550	210	1055	2570
C	I	3000	550	185	1025	2505
	II	2930	535	230	1065	2650
	Mean	2965	545	210	1045	2580
D	I	3115	550	210	1075	2620
	II	2950	530	205	1030	2690
	Mean	3035	540	210	1055	2655
E	I	3120*	575*	160	995	2500
	II	3015	550	195	1060	2555
	Mean	3070	560	180	1030	2530
F	I	3200	560	160	1010	2620
	II	3070	550	210	1085	2635
	Mean	3135	555	185	1050	2630

\* Excluding results for 1 faulty specimen.

the belt length. The thick rubber face was then stripped off by hand as carefully as possible without using any solvent. The thickness of the rubber strips so obtained ranged from 0.200 to 0.209 inch. Each strip was placed in the slide of the buffing machine (see Appendix) and buffed down to a thickness of about 0.10 inch by the method indicated below. Dumb-bell specimens were then cut out from the buffed strip.

The total time occupied in buffing machine (see Appendix) and buffed down to a thickness of about 0.10 inch by the method indicated below. Dumb-bell specimens were then cut out from the buffed strip.

The total time occupied in buffing was kept constant at four minutes, but the procedure was varied as follows, a 36-grit abrasive wheel being used except where otherwise specified:

A: 0.1 inch removed from fabric side by one passage over wheel.

B: 0.1 inch removed from fabric side by 2 passages (0.05 inch by each)

C: 0.1 inch removed from fabric side by 4 passages (0.025 inch by each)

D: 0.1 inch removed from fabric side by 6 passages (0.017 inch by each)

E: 0.05 inch removed from each side by one passage.

F: as A, but finished off with 80-grit wheel.

Tensile tests were made on the day after buffing. The whole set of experiments was later repeated by another operator. Results are given in Table 3, the two sets of experiments being marked I and II. All tensile tests were made at between 65° and 67° F.

Considering the means of the values for sets I and II (see Table 3), the maximum variation in tensile strength, elongation at break, and modulus (excluding that at 100 per cent elongation, which is too small to be accurately measurable) among the six methods of buffing is only about 5 per cent, being in fact of the same order as the difference between sets I and II. There is, moreover, no sign of any continuous variation in properties with the number of buffing operations in the series A-D. It seems to be more than a coincidence, however, that the samples finished off with the fine abrasive (F) give the highest tensile strengths in both sets of tests; this agrees with the results of the earlier tests described in Section 1. On the other hand there is no evidence in the present tests that buffing both sides (E) gives lower tensile strength than buffing one side.

The maximum variation in tensile strength among the four specimens in each test was as follows:

Method	A	B	C	D	E	F
Set I	60	180	90	180	100*	90
Set II	240	180*	90	190	310	50
Mean	150	180	90	185	205	70

\* Excluding 1 faulty specimen.

There is a suggestion, though no more, that the smooth finish on F gives more consistent results and that buffing both sides (E) gives more variable results.

For comparison with the above tests, a set of four specimens was prepared by the hand method used in the experiments described in Section 1, buffing being carried out after cutting the dumb-bell specimens; the results obtained by two operators were as follows:

	TS	EB	M100	M300	M500
I	3025	555	205	965	2490
II	2960	580	205	945	2290
Mean	2995	570	205	955	2390

The only difference from the results obtained with machine-buffed specimens is the slightly higher breaking elongation and lower modulus at 300 and 500 per cent elongation, the reason for which is not evident. The variation in tensile strength among the four specimens (150 lbs. per sq. in. in both sets) is about the same as before.

Buffing by hand did not give quite such uniform thickness over the test-length of the specimen. The variation among the four thickness measurements made on each specimen had the following average values:

Hand-buffed	0.0013 inch (8 specimens)
Machine-buffed	0.00065 inch (160 specimens)



## 3. INFLUENCE OF PERIOD OF TIME OCCUPIED IN BUFFING

In the preceding tests the total period of time occupied in buffing were kept constant at four minutes. Further experiments were therefore made to examine the effect of varying this period. Two sets of specimens were prepared from the thick rubber cover of a conveyer belt by method A of Section 2 above, but taking in one case two minutes and in the other eight minutes for the buffing operation. Results obtained by two operators (I and II) are given in Table 4; all tensile tests were made at 60° F.

TABLE 4

Period of buffing		TS	EB	M100	M300	M500
2 min.	I	3160	555	205	1000	2600
	II	3270	590	225	1030	2610
	Mean	3215	570	215	1015	2605
8 min.	I	3250	560	220	1025	2570
	II	3130	580	205	1035	2570
	Mean	3190	570	215	1030	2570

Judging by these results, variation of the period of buffing does not, within the limits examined, appreciably affect the results.

## 4. INFLUENCE OF REST PERIOD AFTER BUFFING

The object of this series of tests was to discover whether buffing produced any temporary change in the properties of the rubber which was gradually eliminated by allowing the rubber to rest. The time intervals quoted in the

TABLE 5.

Interval between buffing and testing		TS	EB	M100	M300	M500
1 min.	I	3410	550	185	1085	2860
	II	3230	520	205	1260	3005
	Mean	3320	535	195	1175	2935
30 min.	I	3425	560	195	1100	2880
	II	3195	515	205	1265	2975
	Mean	3310	540	200	1185	2930
90 min.	I	3285	530	210	1180	2900
	II	3325	530	200	1235	3045
	Mean	3305	530	205	1210	2975
5 hrs.	I	3220	525	195	1140	2910
	II	3250	525	215	1230	2980
	Mean	3235	525	205	1185	2945
24 hrs.	I	3190	530	200	1240	2880
	II	3030	510	210	1230	2915
	Mean	3110	520	205	1235	2900
72 hrs.	I	3380	540	210	1225	2890
	II	3090	520	205	1180	2975
	Mean	3230	530	210	1205	2930

tabulated results are those between the end of the buffing operation and the beginning of the tensile test.

(i) *Specimens Buffed after Cutting*

For these tests the thin rubber cover of a conveyer belt was used, this being about 0.07 inch thick. The dumb-bell specimens were buffed, using a 36-grit wheel, just enough to remove the cloth marking, thus reducing their thickness to about 0.056 inch. The results obtained by two operators (I and II) are given in Table 5; tensile tests were made at 63–66° F.

There are signs of a slight fall in tensile strength with increasing period after buffing, but the other properties are not affected to any significant extent.

(ii) *Specimens Buffed before Cutting*

Rubber from the thick cover of a conveyer belt was buffed down to about 0.1 inch thick by method B described above (Section 2), using a 36-grit abrasive wheel and a total buffing time of four minutes. Dumb-bell specimens were then cut and tensile tests made at 60° F at various periods after buffing (see Table 6).

TABLE 6

Interval between buffing and testing	TS	EB	M100	M300	M500
1 min.	3260	575	210	935	2450
30 min.	3210	570	165	940	2555
90 min.	3000	545	215	1000	2580
5 hrs.	3110	545	210	960	2630
24 hrs.	3070	530	215	1050	2800
72 hrs.	3040	550	190	895	2545

Excluding the abnormal figure for 90 minutes, there is a steady fall in tensile strength with increasing interval between buffing and testing, amounting to about 7 per cent over the total period. Breaking elongation also shows a tendency to fall. Modulus shows no marked progressive change, though there are signs of an increase up to twenty-four hours.

The fall in tensile strength confirms the indications given by the previous set of tests, paragraph (i). Two possible explanations of this fall suggest themselves, though neither appears entirely satisfactory:

- (a) In buffing stretches the rubber lengthwise, producing a subpermanent decrease in cross-section which gradually disappears during the subsequent rest period, this would cause a gradual decrease in the measured tensile strength of the specimen, assuming that the true tensile strength, calculated on the original unstrained section, does not change during the rest period. The observed fall in breaking elongation, however, cannot be similarly explained.
- (b) The surface left by buffing is, on a microscopical scale, very rough and therefore exposes a large surface to oxidation, a process that may be enhanced by the heating to which the rubber has been subjected during buffing. A thin surface layer on each buffed surface may therefore oxidize and perish relatively quickly, thus reducing the tensile strength of the specimen.

## 5. COMPARISON BETWEEN BUFFED AND UNBUFFED DUMB-BELLS

The experiments were made with the following mix of the tire tread type:

Smoked sheet	100
Sulfur	3.1
Gas black	38
Zinc oxide	7.6
Stearic acid	3.1
Mercaptobenzothiazole	0.78

The stock was vulcanized in a platen press for 60 minutes at 141° C, to give sheets 10 inches square, half of each sheet being 5 mm. thick and the other half 3 mm. thick. From each sheet two standard dumb-bell specimens (5½ in. long, 1¼ in. wide ends, 1 in. × ¼ in. test-length) were cut out of the 3 mm. portion and two strips 6 × 1½ inches out of the 5 mm. portion. All these specimens were taken from as near the middle of the sheet as possible, so as to minimize inequalities in vulcanization. The 6 × 1½ inch strips were buffed down on one side until the thickness was reduced to 3 mm. Buffing was carried out on the buffing machine, using an 80-grit abrasive wheel 6 inches in diameter revolving at 1400 r.p.m. Dumb-bell specimens were cut from the buffed strips.

Several sheets were made, so that after rejecting a few specimens that contained flaws, some fifteen or twenty of each type were obtained. The average thickness of these specimens is shown below together with the average variation in thickness over the test length:

	Thickness	Variation
Unbuffed	0.1178 inch	0.0014 inch
Buffed	0.1186 inch	0.0013 inch

Any observed difference in test results, therefore, cannot be ascribed to a difference in thickness between the two types of specimens or to one type being more uniform over the test length than the other.

After being conditioned for 24 hours at 20° C, the specimens were tested on the Scott machine, with the lower grip travelling at 20 inches per minute. All tests were made on the same day, the test temperature being about 20° C. Results are given in Table 7.

The mean value of each set of results, together with the standard deviation of a single result from the mean, is given below; in the M300 values for unbuffed specimens the figure marked with an asterisk has been omitted from the calculations, because it appears abnormally high and is not accompanied by a correspondingly high value of M500.

	TS	EB	M300	M500
Mean:				
Unbuffed	4395	591	1463	3350
Buffed	4200	575	1428	3345
Standard deviation:				
Unbuffed	217	19	30	105
Buffed	138	11	86*	130

\* Not reliable because the values tend to fall into two groups.

Both tensile strength and elongation at break are lower with buffed than with unbuffed specimens, and in both cases the difference is statistically significant, the odds being about 100 to 1 that the difference is real. In the case

of rigidity there is no evidence that buffing produces a real difference. These effects are, of course, of the kind that would be expected, since buffing produces small surface irregularities and incipient cuts that must weaken the specimen.

It must be noted that the results above relate to the effect of buffing one side only of the rubber; buffing both sides would presumably have at least as great an effect, although the previous results (Table 2, Methods (1) and (3), showed very little difference between specimens buffed respectively on one side and on both sides with a fine abrasive.

TABLE 7

Unbuffed				Buffed			
TS	EB	M300	M500	TS	EB	M300	M500
4630	610	1640*	3410	4480	590	1530	3590
4630	600	1470	3520	4425	580	1570	3600
4580	600	1450	3410	4340	590	1420	3320
4570	620	1420	3240	4340	590	1360	3240
4570	610	1450	3310	4310	590	1380	3340
4540	600	1440	3290	4310	570	1560	3430
4440	590	1490	3500	4240	580	1380	3210
4440	600	1410	3290	4240	570	1430	3380
4350	560	1510	3500	4200	570	1340	3310
4350	590	1450	3260	4190	580	1360	3170
4230	570	1490	3300	4160	580	1550	3400
4220	580	1480	3370	4140	570	1420	3430
4090	580	1460	3170	4140	560	1380	3300
3920	560	1490	3350	4120	550	1590	3510
				4080	570	1350	3340
				4070	580	1360	3100
				4020	560	1390	3370
				4010	570	1340	3270
				3990	570	1420	3290

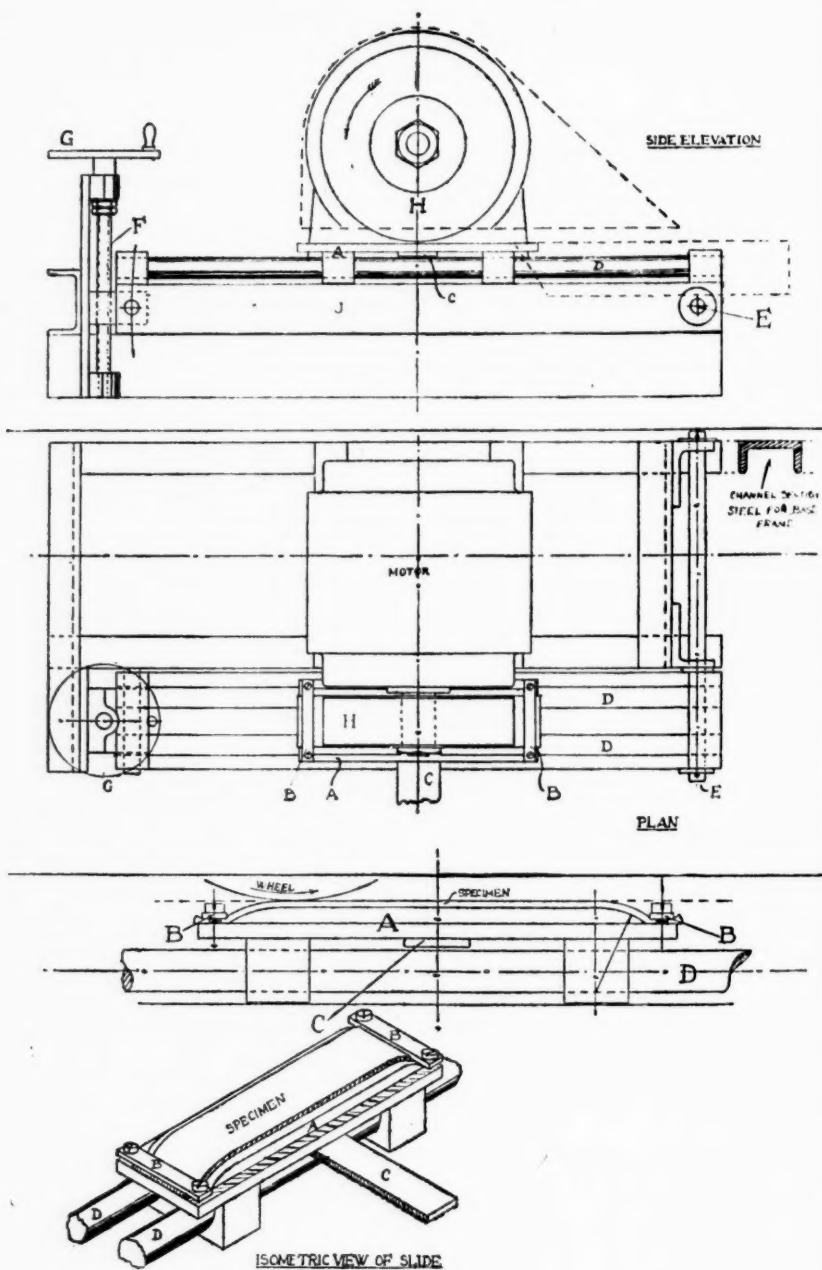
An interesting feature of the present results is that the buffed dumb-bells give more uniform values for both tensile strength and breaking elongation than do the unbuffed dumb-bells, as is evident from the lower standard deviations for the former. The differences in this respect, moreover, appear too great to be ascribed to chance. This result is analogous to the observation of Newton<sup>3</sup> that dumb-bells cut from cloth-marked sheet gave exceptionally uniform tensile strength results, the standard deviation of individual figures from the mean having the unusually low value of 3.26 per cent, which may be compared with the present figure of 3.3 per cent for the buffed dumb-bells.

It appears as if the deliberate introduction of "flaws" on the surface of the specimen, either by buffing or cloth-marking, makes the results more uniform by rendering the break less dependent on the fortuitous occurrence of flaws or variations in the mass of the rubber or flaws in the cut edges.

#### APPENDIX: DESCRIPTION OF BUFFING MACHINE (see Figure)

For the experiments described in Sections 2, 3, 4, and 5, it was necessary to devise an apparatus with which a uniform layer of any desired thickness could be removed from the rubber at each passage under the buffing wheel.

The apparatus used for this purpose comprises a slide or carriage A on which the rubber specimen, in the form of a strip  $7 \times 1\frac{1}{2}$  inches, is held under slight tension by two bars B fixed down by screws. The distance between the outer edges of the bars, BB, is 19 cm. and the overall length of the base is 54 cm.



RUBBER BUFFING MACHINE

(The necessity for applying slight tension might be avoided by making the rubber strip rather wide and holding down its edges by clamping strips.) The ends of the specimen may have to be buffed down previously to prevent the bars from touching the buffing wheel. The slide is provided with a handle C by which it can be slid along the two rods D. The frame J carrying these rods is pivoted at E, while the other end can be raised or lowered by the screw F, fitted with a graduated head G. By rotating G it is thus possible to raise that part of the rubber under the center of the buffing wheel H by any desired amount, and so to remove a layer of the rubber of this thickness when A slides forward under the rotating wheel. This wheel is 6 inches in diameter and  $1\frac{1}{2}$  inches thick, and is mounted directly on the shaft of a  $\frac{1}{4}$  h.p. motor running at 1400 r.p.m. The slide A is moved from right to left. Sheet metal guards, shown in the drawing by dotted lines, are provided to catch the flying rubber dust.

### SUMMARY AND CONCLUSIONS

1. Experiments are described on the influence of buffing vulcanized rubber, before or after cutting into dumb-bell specimens, on the tensile test results obtained with these specimens. The influence of the following factors is examined: fineness of abrasive used for buffing, thickness of rubber removed per passage over the abrasive wheel, total period of contact between the rubber and the wheel, and rest period between buffing and testing.

2. A machine is described for carrying out buffing under controlled variable conditions; this assures the buffed surface being flat and parallel to the under surface of the rubber, and gives more uniform thickness over the test length than buffing by hand.

3. With very soft ("pure") rubbers tensile strength may be reduced as much as 15 per cent by using a coarse abrasive, although with stiffer rubber such as tire treads and conveyer belt covers, this effect is much smaller.

4. It appears to be immaterial whether the rubber removed by buffing is taken off in several thin layers or a few thick ones.

5. Varying the total period of time occupied by buffing within reasonable limits (two to eight minutes in the present tests) does not appreciably affect the test results.

6. With increase in the rest period between buffing and testing, the results indicate a distinct fall in tensile strength and a less marked fall in breaking elongation.

7. Tests on a rubber of the tire-tread type show that, if the dumb-bell specimens have been buffed, even with a fine abrasive that leaves a good surface and taking precautions to ensure uniformity of thickness, the tensile strength is some 5 per cent lower than that of dumb-bells cut from sheets with smooth (moulded) surfaces; the breaking elongation also is correspondingly reduced by buffing. On the other hand, the buffed dumb-bells give more closely concordant results, for both tensile strength and breaking elongation, than the smooth ones.

8. The following recommendations relating to the buffing of rubber for the preparation of tensile test specimens are put forward:—(1) A machine, such as that here described, capable of removing a layer of uniform thickness should be used in preference to holding the rubber by hand against an abrasive wheel. (2) A fairly fine abrasive, say 80 grit, should be used, at least for finishing off the surface. (3) The period during which the rubber is in contact with the



abrasive wheel should be kept as short as possible. (4) The rubber should be buffed down to the required thickness before the dumb-bell specimens are cut. (5) Tensile tests should be made within definite time limits after buffing, say between twelve and forty-eight hours, and the specimens should be cut just before testing, that is, after any subpermanent deformation in the rubber has been largely eliminated.

#### REFERENCES

- <sup>1</sup> Dawson and Porritt, "Rubber: Physical and Chemical Properties", Research Assoc. Brit. Rubber Manufacturers, Croydon, England, 1935, p. 538, Figure 76B.
- <sup>2</sup> See, for example, Reece, *Trans. Inst. Rubber Ind.* 11, 312 (1935).
- <sup>3</sup> Newton, *J. Rubber Research* 14, 113 (1945).